

The
CHEMICAL CONSTITUENTS
of
PETROLEUM

BY

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Preface

The ultimate goal of petroleum chemistry in its analytical aspects is to resolve petroleum into individual hydrocarbons and other constituents. Conspicuous progress along this line has been accomplished during the last ten years owing particularly to the efforts of the National Bureau of Standards.

The problem of separating chemical individuals, quite feasible for petroleum gases, gasolines and perhaps light gas oils, seems to be hopeless for high-boiling fractions, which may contain an innumerable quantity of various entirely unknown hydrocarbons and other compounds. Thus, the separation and quantitative determination of different classes of hydrocarbons and other constituents of petroleum is as important as the separation and identification of individual components.

The hydrocarbons of petroleum are conventionally and broadly classified as paraffins, naphthenes, aromatics and unsaturates. This distinction is quite sharp for low and medium molecular weight hydrocarbons, in which the presence of an aromatic or naphthenic ring or a double bond imparts characteristic properties to these structures. But the classification becomes ambiguous for high molecular weight hydrocarbons, which may contain different structures in one molecule without imparting the characteristic properties of one dominating structure. A high molecular weight hydrocarbon with aromatic and naphthenic rings and long paraffinic side chains would possess paraffinic, aromatic and naphthenic properties to an extent depending upon the proportion of these structures. The ring analysis developed by Waterman obviated these difficulties in a simple and logical manner. The data expressed in terms of ring analysis are of primary importance for characteristics of high-boiling fractions and products, as well as of crude oils.

The wide application of ring analysis, however, does not eliminate determination of the conventional classes of hydrocarbons in petroleum. Ring analysis has its own shortcomings, both of method and of practice. The refiner or chemical manufacturer is interested more in the content of various hydrocarbons and other constituents than in the content of structural fragments. In addition to this, unsaturates, resinous and asphaltic compounds have no part in the ring analysis applied to completely hydrogenated pure hydrocarbons.

The hydrocarbon classes present in petroleum may be classified more specifically as follows.

The paraffins represent the well defined class characterized by the satu-

rated non-cyclic chain structure of hydrocarbons. Other structures are absent in these hydrocarbons.

The naphthenes present in petroleum belong to the saturated five- and six-membered ring hydrocarbons. The presence of other types of naphthenes has not been proved at the present time. The naphthenes are monocyclic in low-boiling fractions and polycyclic in high-boiling fractions.

Like the naphthenes, the aromatics in petroleum are both monocyclic and polycyclic. The classes of naphthenes and aromatics are not so sharply defined as paraffins, because of the presence of rather long paraffinic side chains in these hydrocarbons, as well as of combined naphthenic and aromatic rings. Strictly speaking, the class of naphthene-aromatic hydrocarbons (of varied naphthenicity or aromaticity) should be introduced in the classification. It should be pointed out, however, that even one aromatic ring in a polycyclic petroleum hydrocarbon imparts the aromatic properties, *e.g.*, an abnormal specific dispersion, greater solubility in solvents, capacity for sulfonation, etc. Thus, the aromatic structures present in petroleum may be specified as cyclic hydrocarbons with resonating double bonds, which have the aromatic properties specified above and associated with the presence of one or more aromatic rings in the molecule.

Unsaturation, absent in straight-run fractions, represents an important class of hydrocarbons in cracked products. By "unsaturates" is meant all hydrocarbons which have one (or more) active double bonds in a molecule of any structure, aliphatic or cyclic. The presence of an active double bond imposes its characteristic properties at least on hydrocarbons of low and medium molecular weight, including perhaps those of gas oils. Unsaturation of high molecular weight is almost unknown, and there are no reliable methods of evaluating the content of unsaturates in high-boiling fractions.

The classification of oxygen, sulfur, and nitrogen compounds is simplified in the sense that only comparatively low molecular weight compounds of this kind, well defined chemically, have so far been investigated and identified in petroleum.

By "resinous and asphaltic compounds" is meant all amorphous (non-crystalline) constituents which may contain oxygen, sulfur and nitrogen and which occur mostly in high-boiling fractions.

This rather lengthy preface seems necessary to set forth the views of the author and to justify the handling of the subject in this book. A considerable part of the book is confined to individual hydrocarbons and compounds, which have been separated from petroleum, as well as to the methods of separation and identification. The data on the content of various types of hydrocarbons and other constituents, expressed in the terms of ring analysis and of conventional classes, together with the methods for determining the structures and classes, make up a large part of the volume.

A large literature on the chemical composition of petroleum was used on the basis of its reliability. Many unreliable data have not been included, to avoid an unnecessary criticism (by the author) and an equally unnecessary increase in the size.

The author does not pretend to be an impartial collector of data and views pertaining to the composition of petroleum. Many problems, particularly in the field of chemistry of lubricating oils, petroleum wax, resins and asphaltic constituents, have not been crystallized into commonly accepted theories. The author has not hesitated to take a definite stand on such problems, in the hope that such an attitude may be more useful in stimulating further efforts than an impartial accumulation of the material.

New avenues of investigation are still open in the field of the chemical composition of petroleum. The investigation of coal tar developed the chemistry of aromatic hydrocarbons. It would be premature to predict the achievements which are deemed to be the issue of the investigation of petroleum, a much richer source of hydrocarbons and other constituents than coal tar, which is comparatively poor in the variety and number of its constituents. New methods and conspicuous improvements in classical methods open new possibilities in attacking problems related to the complex composition of petroleum. The enormous complexity of petroleum, though rather a draw-back to investigation today, may become a great stimulus tomorrow.

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A. N. SACHANEN

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April, 1945

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Chapter 1

Petroleum Gases and Natural Gasoline

Petroleum gases are classified according to their origin as (1) natural or casing-head gases, produced in gas or oil fields,* and (2) as refinery gases produced in refineries. The latter are formed as a result of various processes used in refineries, principally that of cracking, which yields the greater part of refinery gases.

Natural-gas gasoline, or better, natural gasoline, is manufactured by absorption or compression of natural gas, which brings about the condensation of hydrocarbons heavier than butanes and to some extent of butanes as well. The same process applied to the refinery gases yields refinery-gas gasoline, similar to natural gasoline, as far as the boiling range and general composition are concerned.

This chapter is confined to the chemical composition of petroleum gases and the light gasolines produced from them.

Methods of Analysis by Fractionation

Analysis of hydrocarbon gases is a comparatively simple operation because of the limited number of constituents present in such gases. In addition to this, the spread between the boiling points of gaseous hydrocarbons is large enough to warrant the use of fractional distillation for their quantitative determination. Any fractionating column equipped for operation at low temperatures containing of about 15 theoretical plates can be successfully used for the quantitative separation of low molecular weight gaseous hydrocarbons, including C_3 and some C_4 hydrocarbons.

The application of fractional distillation to the quantitative determination of hydrocarbon gases is of particular importance, since the classical combustion or explosion method evidently fails to give any data on the content of various hydrocarbons. At the present time fractional distillation of liquefied hydrocarbon gases is a basic analytical method. This method is supplemented by various absorption procedures, particularly for removal of non-hydrocarbon constituents such as hydrogen, carbon dioxide, etc. Various olefins also can be quantitatively separated by selective absorption with sulfuric acid and similar methods.

Erdman and Stoltzenberg¹⁷ were the first to use the condensation of gases at low temperatures for quantitative determination. Such mixtures

*The term "natural" gas is now used as a generic term embracing petroleum gases produced from gas and crude-oil wells; the term "casing-head" gas is more specific, designating petroleum gas produced from crude-oil wells only.

as ethene and hydrogen, ethene and oxygen, carbon dioxide and oxygen, etc., were quantitatively separated by this method. Burrell, Seibert and Robertson⁶ first applied the distillation of liquefied natural gas to the determination of its constituents. Shepherd and Porter⁴⁸ improved somewhat the method of Burrell, but both methods were too cumbersome because of the repeated distillations necessary for a fairly complete separation of hydrocarbons. Podbielniak⁴⁰ made further substantial progress in the technique of the analysis of gaseous hydrocarbons by introducing a rectifying column. As a result, the quantitative separation of hydrocarbons was obtained in a single fractionating operation.

The distilling bulb of the Podbielniak apparatus is directly connected with the fractionating column (height 85 cm, diameter $2\frac{1}{2}$ to 4 cm) which has the wire spiral packing. This packing is widely used in laboratory columns; it gives a fairly efficient fractionation with minimum hold-up (Chapter 2). The distilling bulb and fractionating column are vacuum-jacketed, and the distillation bulb is provided with an external or internal resistance wire for heating which is controlled by a rheostat. The distilling bulb has an inlet for the introduction of the gas to be analyzed. The top of the fractionating column is a reflux chamber cooled by a refrigerant, which is kept in an annular container surrounding the top of the fractionating column. The reflux chamber is provided with a thermocouple.

The procedure of the analysis is as follows. The gas is freed of water vapors and carbon dioxide, which would freeze in the apparatus. These are removed by conventional methods. However, when olefins are present, magnesium perchlorate trihydrate is used for the removal of water vapors to avoid the use of conventional drying reagents which may react with olefins.

The apparatus is evacuated before the analysis up to the residual pressure of 2 mm or less. The sample of gas to be analyzed is usually precooled to the condensation temperature and then introduced into the distilling bulb, which is cooled with liquid air. The volume of the gas sample is about 6 liters. A part of the sample is vaporized, thus increasing the pressure in the apparatus. By heating the distilling bulb, the pressure in the apparatus is brought close to atmospheric. Simultaneously the proper cooling of the reflux chamber by liquid air in the annular container produces a necessary amount of reflux which should be sufficient to moisten the entire wire packing.

The heating of the sample in the distilling bulb and the reflux formation should be so balanced that the pressure in the apparatus is practically atmospheric. The valve between the reflux chamber and the receiver is closed, and no distillate is withdrawn in this stage of the operation, corresponding to the total reflux. When equilibrium has been established, fractionation is started. The gases and vapors from the reflux chamber are conducted to the receiver which has previously been evacuated to a low pressure. The rate of distillation, controlled by the valve, is meas-

ured by the rise in pressure in the receiver, which is provided with a special manometer. The temperature at the top of the rectifying column is recorded in millivolts. The reflux ratio is from 10 to 15; no overflowing is permissible. The fractionation of permanent gases and hydrocarbons, including propane, is carried out at atmospheric pressure; that of butanes at a pressure of 400 mm; and that of heavier hydrocarbons at a pressure of 200 or 300 mm.

The vapor temperature corrected to atmospheric pressure is plotted against the amount of vapors obtained. The curve consists of plateaus corresponding to individual hydrocarbons and very sharp vertical curves, particularly for low molecular weight hydrocarbons, which show a sharp separation effect. The separation is obviously much less sharp for C_4 and C_5 hydrocarbons, which have comparatively small spreads between boiling temperatures. The determination of the total content of C_5 and heavier may involve a considerable error, if the total content of these hydrocarbons is relatively small.

McMillan³¹ slightly modified the Podbielniak columns by improving the spiral packing. The packing in these columns consists of a six-turn-per-inch No. 13-gage brass spiral wire with a No. 23-gage straight-wire insert. McMillan's packing is being used in the California Natural Gas Association's columns.

The new Podbielniak columns⁴¹ have a more efficient packing than the spiral. The Heli-Grid packing used in such columns is described in Chapter 2. The number of theoretical plates in the new Podbielniak columns is 50 or more compared with 12 in the early apparatus. The operation is substantially automatic. The close separation of isobutane from isobutene and butene-1, and of the latter from *n*-butane and butenes-2 is feasible with these columns.

Ward⁵⁸ developed the apparatus of Shepherd and Porter. The separation of hydrocarbons is carried out by a series of distillations in four or more condenser tubes at pressures below 0.1 mm mercury.

The latest modifications of the method give very reliable results for the separation of gaseous hydrocarbons, the deviations being close to 0.5 per cent or less on the average. The separation of such hydrocarbons as, for instance, isobutane from isobutene involves greater deviations. A comprehensive comparison of the various modifications mentioned above has been made by Savelly, Seyfried and Filbert.⁴⁷

There are new methods of quantitative determination of various hydrocarbons in gases, based upon the absorption of infrared rays, Raman effect and the ionization of gases.^{27, 57} These will be described in Chapter 2. The infrared and Raman methods are applied mostly to narrow fractions, for instance, for determination of normal butane and isobutane in C_4 fractions. The accuracy of these methods is very satisfactory (about $\frac{1}{2}$ per cent), and the procedure requires only about 15 minutes and a few cc of the sample.

The analysis by mass spectrometry gives fairly accurate results. The

deviations for various hydrocarbons in synthetic mixtures are of the order of 1 per cent.

In addition to the general analytical methods described, which can be applied to any hydrocarbon gas, some special methods may be used for analysis of certain fractions, particularly for determining the components of C_4 fractions.

In the fraction containing only saturated butanes, the determination of normal and isobutanes can be successfully carried out by the so-called dew-point method described by Woog, Sigwalt and Gomer.⁵⁰ A sample of a gaseous mixture of butanes is introduced into an apparatus at 0°C under reduced pressure. The pressure then gradually increases, resulting in a corresponding decrease in the volume of the sample. The decrease in volume is slow up to the dew point, after which it is rapid. Thus, the dew point can be determined by plotting the volume contraction versus pressure. The mole per cent of isobutane is calculated on the basis of the volume per cent of isobutane at 0°C and the total pressure at the dew point. The determination of isobutane in the C_4 fraction by this method gives reliable figures only under the condition that the fraction does not contain any other hydrocarbons.

Another method is based on the orthotoluidine points of the C_4 fractions and will be described in Chapter 2.

Determination of Olefins

If the hydrocarbon gas contains olefins, the quantitative determination of all constituents by fractional distillation becomes difficult, particularly for C_4 and C_5 fractions. Complete analysis of the latter, which contains paraffins and olefins, has not been attained.

The determination of olefins is carried out by absorption with sulfuric acid or bromine, or by hydrogenation. The olefins may be determined in the total gas as well as in the separated C_2 , C_3 , C_4 and C_5 fractions.

In the first method the use of fuming sulfuric acid should be avoided because of the reaction of the acid with C_3 and C_4 paraffinic hydrocarbons. However, the concentration of sulfuric acid should be high (about 98 per cent), since ethene reacts slowly with less concentrated sulfuric acid. It is recommended to dissolve silver sulfate or nickel sulfate, or both, in concentrated sulfuric acid up to saturation to increase the activity of the acid.

In the second method a weak bromine solution, *e.g.*, 1 per cent of bromine in 3 to 5 per cent of aqueous potassium bromide, is used. Suida and Wesely⁵¹ recommend decreasing the concentration of bromine to 0.04 per cent to avoid any side reactions. Exposure to sunlight, as well as the use of concentrated bromine solutions, should be avoided to eliminate the side reactions, *e.g.*, bromination of paraffin hydrocarbons. Hydrogen sulfide and butadiene react with bromine and must be removed before the treatment.

Stanerson and Levin⁵⁰ titrate the olefins present in hydrocarbon gases by a solution of bromine in glacial acetic acid. This method is practically the determination of bromine number described in Chapter 3.

The difference in the activity of ethene toward sulfuric acid as compared with that of propene and butenes is used for quantitative determination of ethene. The gas to be tested is absorbed with 87 per cent sulfuric acid, which readily absorbs propene and butenes and does not attack ethene, at least if the concentration of ethene is not particularly large. After propene and butenes have been removed, the gas is treated with 98 per cent sulfuric acid in the presence of silver sulfate or nickel sulfate for absorption of ethene.

Eberl¹⁴ showed, however, that 72 per cent sulfuric acid containing 6 grams of silver sulfate per 100 cc absorbs ethene quantitatively. The use of this reagent is preferable to that of concentrated sulfuric acid, which may attack paraffins, particularly isobutane. This reagent may evidently be used for the total absorption of olefins with the same advantage.

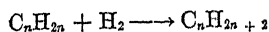
The percentage of isobutene, which is particularly reactive, can be determined by treating the gas with 50 to 60 per cent sulfuric acid. At this concentration the acid reacts only with isobutene and does not attack other olefins. In the presence of butadiene the concentration of sulfuric acid should be not more than 50 per cent, to prevent its reacting with butadiene. It should be pointed out, however, that the reaction between isobutene and 50 to 60 per cent sulfuric acid is very slow.

The separation of propene from normal butenes by the use of sulfuric acid in various concentrations is impractical because of the closeness of the rates of reaction of these hydrocarbons.¹⁹

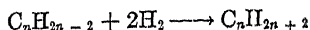
It should be kept in mind, however, that some interaction is possible between concentrated sulfuric acid and paraffins, particularly isobutane; therefore, the figures of the content of olefins obtained by the use of concentrated sulfuric acid are to be considered approximate. Matuszak³⁰ made a comprehensive survey of the methods using sulfuric acid for separation of various olefins.

The McMillan method³² for the determination of isobutene by selective reaction with anhydrous hydrogen chloride is to be preferred to absorption with sulfuric acid. The reaction is quantitative at room temperature and does not involve other C_4 unsaturates. The paraffins are not attacked by this reagent.

McMillan, Cole and Ritchie³³ described the determination of the olefins either in total gas or in fractions by hydrogenation. A measured volume of hydrogen is mixed with a known quantity of the gas, and the mixture is passed over a nickel catalyst at room temperature and atmospheric pressure. The nickel catalyst on asbestos is prepared by soaking the asbestos with melted crystalhydrate of nickel nitrate, by calcination and reduction with hydrogen at 325°C. The volume percentage of olefins equals the contraction of the volume after hydrogenation:



or, in the case of butadiene or acetylene, to one-half of the contraction:



The calculations of the volume contraction are based on the assumption that the hydrocarbons in question are ideal gases. The effect of deviations from the ideal state and corrections is discussed by Robey and Morrell.⁴³ If butadiene and acetylene are present, they are determined separately, and suitable corrections are applied for the calculation of the percentage of olefins.

In the presence of carbon monoxide the temperature of absorption of hydrogen is increased to 180°C because of the retarding effect of carbon monoxide on hydrogenation; or carbon monoxide may be removed before hydrogenation. The hydrogenation method is much more accurate than the sulfuric acid method because of the absence of any side reactions which may involve paraffins.

The analysis of butane-butene or B-B fractions is of particular commercial importance. The complete analysis of such fractions requires the use of efficient columns, such as Podbielniak Heligrad, etc. Even with these columns the separation of isobutene and butene-1, or normal butane and butenes-2, is impossible. The chemical methods described above are used in addition to the fractionation method.

The most widely used technique for separating constituents of B-B fraction starts with a preliminary separation in the efficient column of C_4 hydrocarbons into two fractions. One of these includes isobutane, isobutene, butene-1, and butadiene-1, 3 (boiling range from -12.2° to -5°C); the other includes *n*-butane and butenes-2 (boiling range from -0.5° to 3.7°C). In the first fraction isobutene is determined by absorption with dilute sulfuric acid or, better, with hydrochloric acid; butadiene by adsorption with maleic anhydride (see below); the total amount of the unsaturates by hydrogenation; and isobutane by difference. In the second fraction, butenes-2 are determined by hydrogenation and *n*-butane by difference.

The determination of three isomeric butenes is very involved because of the similarity in their chemical properties. Frey and Yant²⁹ applied the following procedure. *Cis*-butene-2 is the most reactive of the three isomers and can be removed rather completely by reaction with 70 per cent sulfuric acid. The remaining *trans*-butene-2 and butene-1 are brominated, and the dibromides formed are heated in a sealed tube at 100°C with 15 per cent alcoholic potassium hydroxide for 2 to 5 hours. The brominated butene-1 is converted to the extent of 51 per cent into ethylacetylene which is determined in the form of a double compound with silver nitrate.

The preliminary separation of butene-1 by fractionation with an efficient column would simplify the method described. Thus, the treatment of the fraction containing normal butane and butenes-2 with 70

per cent sulfuric acid would be sufficient to evaluate the percentage of *cis*-butene-2.

Determination of Butadiene and Acetylene

There are two methods for the quantitative determination of butadienes. The first involves bromination of the gas to be tested by passing it through bromine and water. As a result, a series of dibromides of olefins and tetrabromides of butadienes is formed. Tetrabromides of butadienes have maximum boiling points and are separated by distillation of the dibromides up to 130°C at 20 mm pressure. The residue contains butadiene tetrabromides, which are crystallized from alcohol.²⁹ By this method the total butadiene-1, 2 and butadiene-1, 3 is determined.

The method suggested by Tropsch and Mattox⁵⁴ is used for determination of butadiene-1, 3. It is known that the conjugated dienes react with maleic anhydride to form condensation products (Chapter 3). The reaction between maleic anhydride and butadiene-1, 3, however, is very slow. Tropsch and Mattox absorb butadiene in molten maleic anhydride at 100°C, under which conditions the rate of condensation is fairly high. A small quantity of maleic anhydride, 2 to 2½ grams, is used for this purpose. The reaction is selective; olefins do not react under these conditions. Robey, Morrell, and Vanderbilt⁴⁴ found, however, that isobutene, particularly in concentrations of 10 per cent or more, is also absorbed by molten maleic anhydride. The remedy is to add 2 to 3 per cent of a high-boiling primary or secondary amine to the maleic anhydride, which inhibits the undesired reaction between the anhydride and isobutene (see Chapter 3).

Cunco and Switzer⁹ determine butadiene (in the absence of acetylene) by total absorption of all unsaturated hydrocarbons by mercuric nitrate solution and by hydrogenation. The mol per cent of butadiene equals the mol per cent unsaturation by hydrogenation minus the mmol per cent unsaturation by mercuric nitrate absorption. The results are claimed to be close to those obtained with maleic anhydride.

Acetylene is not present in ordinary cracking gases, but it may occur in the gases produced at very high temperatures above 700°C (1292°F). The determination of acetylene in the presence of other unsaturated hydrocarbons and carbon monoxide is a difficult problem. Many data on the occurrence of acetylene in some cracked gases are erroneous because of the use of reagents which react with olefins, particularly ethene, or carbon monoxide. Lebeau's reagent (30 grams of potassium iodide, 25 grams of mercuric iodide in 100 cc of water, with the addition of a small quantity of potassium hydroxide) seems to be the best, as it reacts more or less selectively with acetylene.

Desorption

A comparatively new method of the analysis of gaseous hydrocarbons is that of desorption, described by Peters and Lohmar,³⁰ Edse and

Harteck,¹⁵ and Harteck and Suhr.²⁴ The gas is adsorbed by activated charcoal at an extremely low temperature (about -185°C). One gram of activated carbon is used for adsorption of 15-50 cc of gas. When the adsorption is complete, the gas is slowly desorbed at gradually increased temperatures and measured. The composition of fractions and the temperatures of desorption are given in the following table:

CH_4	-185°C	$i\text{C}_4\text{H}_{10}, n\text{C}_4\text{H}_{10}$	$+60^{\circ}$
C_2H_6	-80°	$n\text{C}_4\text{H}_{10}, \text{C}_5\text{H}_{10}$	$+100^{\circ}$
$\text{C}_2\text{H}_6, \text{C}_3\text{H}_8$	-21°	C_6H_{10}	$+160^{\circ}$
$\text{C}_3\text{H}_8, i\text{C}_4\text{H}_{10}$	0°	C_8H_{14}	$+350^{\circ}$
$i\text{C}_4\text{H}_{10}$	$+20^{\circ}$		

In the presence of olefins the above procedure may be used, and the olefins are determined in each fraction by the chemical methods. In another modification the gas is hydrogenated, and the procedure described

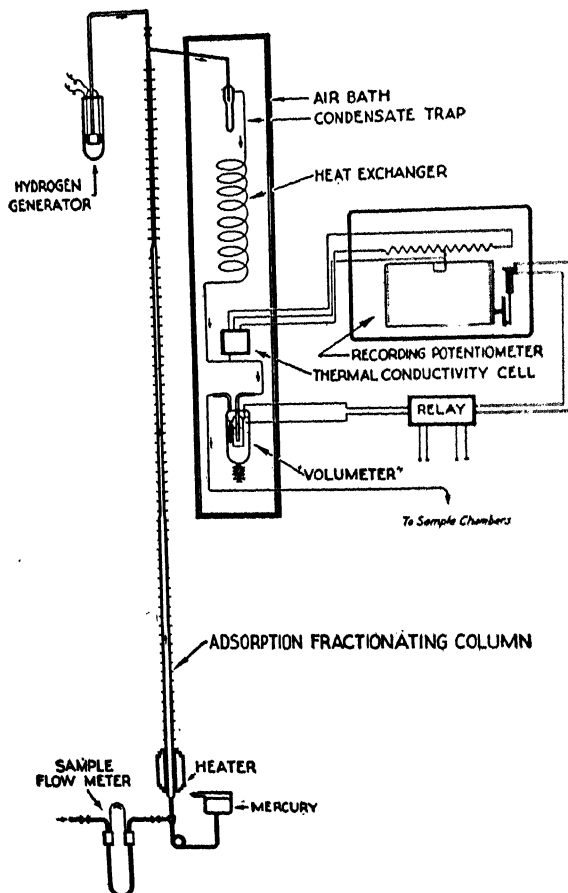


FIGURE 1. Desorption apparatus. (Courtesy Petroleum Refiner)

is then applied. Another portion of the gas is treated with sulfuric acid for absorption of olefins, and the gas so treated is adsorbed and desorbed according to the method in question. The percentage of olefins is calculated by difference between the figures obtained for the hydrogenated and the sulfuric acid-treated gas.

Turner⁵⁵ described another modification of the desorption method. The gas is processed in a column 6 feet long, the inside diameter of which tapers from $\frac{3}{4}$ inch at the bottom to $\frac{3}{16}$ inch at the top (Fig. 1). The column is packed with activated carbon. The sample of gas is introduced into the bottom of the column at room temperature. Then the heater is run until its temperature reaches 750°F. At this point the heater gradually rises to the top of the column. This operation lasts about 8 hours. The gradual desorption of the adsorbed gas occurs during this time, and the gas liberated is driven out by the rising mercury level. On reaching the top, the heater remains stationary for 20 minutes, during which time hydrogen is used for removal of the last portion of the gas.

The following fractions are quantitatively separated:

air	isobutane
methane	<i>n</i> -butane, isobutene, butene-1
carbon dioxide	butene-2, butadiene
ethene	isopentane
ethane	<i>n</i> -pentane
propane and propene	

Such hydrocarbons as propane, propene, etc. cannot be separated by this method and obtained in the same fraction.

Determination of Non-hydrocarbon Constituents

The separation and quantitative determination of other constituents of hydrocarbon gases is performed by conventional methods.

Carbon dioxide and hydrogen sulfide are separated by reaction with concentrated (60 per cent) potassium hydroxide. The relative amount of hydrogen sulfide can be determined by titration of the gas with iodine-potassium iodide solution in the presence of starch. The concentration of iodine in the solution corresponds approximately to 0.01*N*. The methods for determination of mercaptans are described in Chapter 8.

Oxygen, which does not occur in any pure petroleum gas, can be frequently found, however, as a result of the intrusion of air. The determination of oxygen is routine. Uhrig, Roberts and Levin⁵⁶ discussed the methods of determination of small quantities of oxygen in hydrocarbon gases.

Carbon monoxide is absorbed in an ammonia solution of cuprous chloride (75 grams of cuprous chloride and 25 grams of ammonium chloride in 180 cc of distilled water are diluted with concentrated aqueous ammonia until complete dissolution takes place, in the absence of air).

Hydrogen is selectively absorbed by the palladium-asbestos method (Hempel) at room temperature or by a colloidal solution of palladium at 50°C (Paal and Hartman method⁵⁸). A modification of this process is

absorption by palladium sponge activated by heating to a dull red heat in air. The temperature of absorption is 100°C. The unsaturates must be removed before absorption takes place.

McMillan *et al.* apply the hydrogenation method described above to the determination of hydrogen in any hydrocarbon gases which are free from unsaturates. Any pure olefin is mixed with the gas to be tested, and the contraction of the volume after hydrogenation is equal to the volume of hydrogen in the gas.

Nitrogen is determined quantitatively by complete combustion of the gas, either in a combustion pipette¹¹ or with copper oxide.¹¹ The combustion products are absorbed by concentrated solution of potassium hydroxide and the excess of oxygen by an alkaline solution of pyrogallol. The volume of the residue unabsorbed is nitrogen, which may also contain helium.

In the earlier work nitrogen was separated from helium by passing the gas over hot magnesium or calcium carbide. These substances react with nitrogen at high temperatures to form solid, stable magnesium nitride or calcium cyanamide. At the present time a much more convenient method is in use, which utilizes the fact that all gases except helium (and other noble gases, if present) are absorbed by activated carbon at the temperature of liquid air.²¹

Oil-field (Natural) Gas

The composition of oil-field or natural gases may vary between broad limits. The oil-field gases may contain paraffin hydrocarbons, water vapor, nitrogen (including helium), carbon dioxide, and hydrogen sulfide with mercaptans. Paraffin hydrocarbons are represented by methane, ethane, propane, butanes and heavier paraffins, the low molecular weight hydrocarbons being largely predominant. A very small proportion of low-boiling naphthenes and even aromatics may also be present in rich gases. Olefins, carbon monoxide, hydrogen and oxygen are absent in natural gas. Oxygen, however, is frequently found in natural gas due to the intrusion of air. It is not improbable that carbon monoxide may be present in some natural gases in very small quantities.

The proportion of non-hydrocarbon constituents, *i.e.*, water vapor, nitrogen, carbon dioxide and hydrogen sulfide, is usually so small that natural gas may be said to consist chiefly of paraffin hydrocarbons. The maximum amount of water vapor in natural gas at room temperature corresponds to saturation, or to 2.5 per cent by volume. In some cases natural gas may be almost pure nitrogen or carbon dioxide. For instance, some wells of Mexico, New Mexico, and Colorado produce gas containing as much as 90 to 95 per cent of carbon dioxide. The natural gas of some wells of Kansas contains 80 per cent or more nitrogen. The presence and the content of helium is usually related more or less closely with that of nitrogen. The maximum proportion of helium in certain Mid-Continent natural gases reaches 1 to 2 per cent.

The content of hydrogen sulfide, usually very low, may be as high as from 5 to 10 per cent by volume, as in some gases of Iran or the Texas Panhandle. Mercaptans also have been found in some gases in appreciable quantities.

The proportion of individual paraffins varies widely in different gases. "Dry" natural gas consists predominantly of methane and ethane. The content of methane in certain natural gases may be as high as 99 per cent. "Wet" natural gas contains a large proportion of propane, butanes and heavier hydrocarbons; the total amount of these may be 50 per cent by volume or more. Normal butane usually predominates over isobutane, as will be seen later.

From the commercial standpoint the content of butanes and heavier components is the most important quality of a natural gas, as it predetermines the yield of natural gasoline. This yield is customarily referred to per thousand cubic feet, indicating how many gallons of natural gasoline are produced from this volume of gas. The yield varies from zero to 0.5 gal from dry gases and is from 0.5 to 5.0 gal or more from wet gases.

The content of butanes and heavier fractions, *i.e.*, the yield of natural gasoline, depends upon many factors, the most important of which are as follows:

(1) The properties of the crude oil. Those of high A.P.I. gravity and rich in low-boiling constituents give natural gases rich in these constituents or in natural gasoline, and *vice versa*.

(2) The temperature of crude oils in oil deposits. The temperature of crudes *in situ* varies greatly, from 25°C (77°F) to 120°C (248°F). Obviously the natural gas which accompanies a hot crude oil will be particularly rich in natural gasoline. The temperature of Grozny crude oils *in situ* exceeds 100°C, and the content of natural gasoline in such oil-field

Table 1. Average Gas-crude Oil Ratios of Some Oil Fields.*

Field	Gas-crude Oil Ratio (cu ft per barrel)	Field	Gas-crude Oil Ratio (cu ft per barrel)
Dominguez, Cal.	1,968	Monument, N. Mex.	3,048
Huntington Beach, Cal.	1,230	Rodessa, Texas	3,127
Inglewood, Cal.	627	Conroe, Texas	250
Long Beach, Cal.	1,074	Hastings, Texas	400
Santa Fé Springs, Cal.	787	Goldsmith, Texas	1,864
Seal Beach, Cal.	703	Yates, Texas	217
Wilmington, Cal.	423	Russia, Baku (Surachany)	5,000
Ventura Ave, Cal.	2,863	Russia, Baku (Balachany)	3,000
Kettleman Hills, Cal.	4,480	Russia, Grozny	120
Rodessa, La.	4,481	Persia, Masjid-i-Suleiman	240
Eunice, N. Mex.	5,040	Persia, Haft Kel	520
Hobbs, N. Mex.	2,283	Persia, Naft-i-Shah	1,020

*Data for U. S. crude oils from Miller and Shea.³⁵

gases exceeds 5 gallons per 1,000 cu ft. It should be mentioned also that Grozny crude oils contain up to 30 per cent of gasoline.

(3) Pressure of the natural gas *in situ*, which may vary from 50 to 3,000 lbs per sq in or more. Other conditions being equal, the higher the

pressure *in situ* the more natural gas is dissolved in crude oil, or the leaner the gas, and *vice versa*.

(4) Pressure of the natural gas in a separator, which varies from atmospheric to about 100 lbs per sq in. Lindsly,²⁸ for instance, gives the following data on the composition of a casing-head gas (Oklahoma City crude) from two separators under 265 and 16 pounds pressure:

Pressure (lb/sq in)	Methane	Ethane	Propane	Butanes	Pentanes and Heavier
265	87.3	7.9	3.0	1.8	
16	60.4	16.9	13.8	6.3	2.6

(5) Ratio of gas to crude oil. This ratio varies from 100 to 6,000 cubic feet per barrel as the data of Table 1 show. Other conditions being equal, the greater the ratio the leaner the gas, and *vice versa*. The gas fields produce gas only so that the ratio algebraically is infinite. Accordingly, the natural gas of gas fields is very poor in natural gasoline, as has been mentioned above.

(6) The age of the well or of the whole oil stratum. An old well or stratum produces gas richer in natural gasoline because of the gradual decrease of the pressure and of the gas-oil ratio.

Specific gravity of natural gas, as well as heat of combustion, are directly related to the composition of gases. As a matter of fact, both properties are additive and can be calculated on the basis of the per-

Table 2. Composition of Natural and Oil-field Gases.

Field	Spec Grav (air = 1.00)	Per Cent by Volume							
		N ₂	CO ₂	H ₂ S	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂ ^a
Ave Pa. dry	0.65	2			85	8	4	1	
Ave Pa. wet	0.90	1			60	16	12	8	3
Ave Okla. dry	0.65				85	9	4	2	
Ave Okla. wet	1.0	1			45	25	17		4
Ave Kansas dry	0.60	5			94	1			
Kansas, rich in N (Augusta)	0.95	88*			10	2			
Ave Texas dry	0.60	2			89	3			
Texas, rich in N (Petrolia)	0.83	38†			51			11	
Ave W. Va. dry	0.70				82	10	5	2	
Ave W. Va. wet	0.95				59	18	13	6	
Ave La. dry	0.60				92½	4	2	1	
Ave Calif. dry	0.65	2	10		87	1			
Ave Calif. wet	0.85	2	5		68	9	8	5	3
Portero, Mexico ¹²	1.16		14.0	4.5	36.0	20.0	12.0	7.0	6.5
Poza Rica, Mexico ¹²	0.93	0.1	16.3		64.5	5.4	7.8	3.6	2.3
Baku, Russia ¹²	0.57		2.3	0.01	82	0	0	0	0.1
	to		to	to	to	to	to	to	to
	0.70		13.0	0.1	97	3	1	1.4	2.2
Grozny, Russia	1.24				47.6	10.4	17.3	17.3	7.5
Maikop, Russia	1.05	6.9			53.6	14.2	11.7	8.2	5.4
Masjid-i-Suleiman, Iran ¹²	1.06								
				10.4	45.3	13.5	15.3	10.8	4.7

*Including 1 per cent helium.

†Including 2 per cent helium.

centage of various components of the gas. The specific gravity of natural gas varies from 0.55 (pure methane) to 1.50, very rich gas containing about 8 gal of natural gasoline per 1,000 cubic feet; the heat of combustion (calorific value) varies from 1,000 to 2,500 Btu per cubic foot.

Table 2 contains some classified data on the composition of natural gases of the most important oil fields. It should be mentioned, however, that the composition of natural gas from the same well or stratum may vary within certain limits, depending upon the pressure, age of the well etc., as has been mentioned above.

If a natural gas is subjected to compression or absorption in producing natural gasoline, the residual gas leaving the unit will be leaner than the original gas. The difference in the composition of the inlet and outlet gas depends obviously upon the content of heavier condensable hydrocarbons, as well as upon the degree of condensation. Table 3 gives some data on the effect of the extraction of a natural gas (winter).

Table 3. Composition of Inlet and Outlet Natural Gas from Gas Absorption Unit.

	Spec grav (air = 1)	-Per Cent by Volume-				
		Methane	Ethane	Propane	Butanes	Pentanes and Heavier
Inlet gas	0.98	49.5	25.4	16.7	6.2	2.2
Outlet gas	0.78	63.6	27.9	7.2	1.3	0.0

Cracked Gases

Cracked gas is produced in all cracking operations. The yield depends upon many variables, such as the nature of the charging stock, temperature, time and pressure of cracking. The average yield of cracked gas is close to 500 cubic feet per barrel of charge from gas oils, processed in the mixed-phase, non-catalytic residuum process with maximum yield of gasoline (about 60-65 per cent). In the catalytic process (clay as a catalyst) the yield of cracked gas is lower, and does not exceed 200 cubic feet in one-pass operation (yield of gasoline is about 45 per cent). Vapor-phase cracking produces an average of 1,500 cubic feet of gas per barrel of charge for a maximum yield of gasoline in the residuum process, because of much more severe cracking conditions. The yields of cracked gases sharply decrease with decreasing yield of gasoline, and *vice versa*. Thus the non-residuum process, yielding maximum gasoline, coke and gas, gives up to 1,000 cubic feet of gas per barrel of charge.

The chemical composition of cracked gases differs substantially from that of field gases. The cracked gases do not contain nitrogen and carbon dioxide, but are comparatively rich in olefins. Hydrogen also occurs in cracked gases, usually in low percentages.

As in the case of oil-field gases, the chemical composition of cracked gases obtained in the same process depends upon the conditions under which the gas is separated from the liquid constituents. Thus receiver gases—those directly produced from cracking units—differ substantially from stabilizer gases. They are of low specific gravity and are rich in methane. On the other hand, the properties of receiver gases depend upon

the pressure of condensation. Such units as the Holmes-Manley or Dubbs, which employ high pressure for the condensation of gasolines, give cracked gases of lower specific gravity than the gases of other systems, where condensation takes place under low pressure.

The marked effect of the pressure of condensation upon the chemical composition of cracked gases may be illustrated by some data of Egloff and Morrell¹⁶ given in Table 4.

Cracked gases of high specific gravity (1.3 and up) are obtained from the stabilization units as unstable (with regard to evaporation losses) constituents of cracked gasolines. They are rich in high molecular weight gaseous hydrocarbons, particularly C_3 and C_4 . It should be remembered that unstable gasolines contain a considerable proportion of dissolved C_3 and C_4 hydrocarbons, which are separated in the process of stabilization as an overhead distillate and gas. The average percentage of the stabilizer gas depends on the condensation pressure, and is close to 30 to 40 per cent of the total gas produced in cracking.

The difference between receiver gases from cracking units and gases from stabilizers is illustrated in Tables 5 and 6 for mixed-phase¹⁶ and vapor-phase²⁶ processes.

Table 4. Chemical Composition of Receiver Cracked Gases vs. Condensation Pressure.

Charging Stock: Mixture of Fuel Oil, Gas Oil and Wax Distillate.

Temperature 495°C (925°F). Pressure 250 lbs/sq inch.

Condensation Pressure (lbs/sq in)	H ₂	CH ₄ + N ₂	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂	C ₆ H ₁₄	C ₇ H ₁₆	C ₈ H ₁₈
30	0.67	9.4	24.77	2.18	30.68	15.24	7.7	30.68	4.81
250	2.00	64.48	16.06	2.75	6.75	1.90	2.93	6.75	trace

Table 5. Chemical Composition of Cracked Gases from M.C. Kerosene Distillate, Produced in Mixed-phase Process.

Temperature 510°C (950°F). Pressure 400 lbs/sq inch.

	Receiver 30 lbs/sq in	Stabilizer
Hydrogen and methane	53.0	11.3
Ethane	20.6	18.6
Ethene	4.4	2.2
Propane	8.7	19.5
Propene	7.0	14.5
Butanes	3.1	10.3
Butenes	1.9	7.6
Butadiene		6.9?
Heavier	9.1	

Table 6. Chemical Composition of Cracked Gases from Gulf Coast Crude, Produced in Vapor-phase Cracking.

	Receiver	Stabilizer
Methane and hydrogen	38.81	11.37
Ethane	13.15	12.35
Ethene	20.31	15.56
Propane	3.68	
Propene	13.15	44.87
Butanes	6.43	13.86
Butenes		
Higher	2.47	1.99

Under the same cracking conditions, the chemical composition of cracked gases depends upon the charging stock to a comparatively slight extent. The data of different experimenters on the composition of cracked gases from various stocks are usually not comparable, since the difference in the pressure of condensation and in other conditions affects the composition of gases to a greater extent than does the difference in the cracking stocks. Tannich, Thomas and Padgett⁵² give the data on the composition of cracked gases obtained by the same process (Tube-and Tank) at approximately the same temperature, from 900° to 1,000°F, and the same pressure, 750 pounds (Table 7).

Table 7. Composition of Gases Produced by Cracking of Various Stocks.

Cracking Stock Components (% by vol)	Naphtha (reforming)	Process Gas Oil	Recycle Gas Oil	Residuum
Methane, etc.	42.9	36.4	36.5	42.6
Ethane	17.9	21.8	18.4	22.1
Ethene	2.7	2.0	5.9	1.6
Propane	16.3	19.4	13.8	19.1
Propene	6.5	2.9	10.0	1.4
Isobutane	5.0	2.7	2.4	1.7
Isobutene	2.3	0.7	2.1	0.6
n-Butanes	2.9	7.1	3.4	5.7
n-Butenes	1.3	2.1	3.0	2.0
Pentanes	0.9	2.4	1.6	1.2
Pentenenes	0.8	1.4	1.8	2.0
Heavier	1.8	1.1	1.1	
	100.0	100.0	100.0	100.0
Unsaturates	13.6	9.1	22.8	7.6

The olefin content, particularly ethene and propene, is considerably greater for recycle gas oil, but it would be premature to draw any general conclusions on the basis of insufficient data.

Cracking conditions very greatly affect the chemical composition of cracked gases. High cracking temperature favors the formation of hydrogen and olefins. High pressure is favorable to polymerization of olefins. Thus the gases of the vapor-phase process are richer in olefins and hydrogen than those of the mixed-phase. Tables 8 and 9 give data on the average composition of the cracked gases resulting from these two processes.

Table 8. Average Chemical Composition of Cracked Gases Produced in the Mixed-phase Process (% by vol.).

Specific Gravity (air = 1) from 0.8 to 1.0.

	Low-pressure Condensation About 50 lbs/sq in	High-pressure Condensation About 200 lbs/sq in
Hydrogen	1	3
Methane	40	65
Ethane	16	16
Ethene	3	3
Propane	21	5
Propene	9	4
Butanes	5	2
Butenes	4	2
Heavier	1	
Olefins	16	9

The average data of Table 8 relate to the modern mixed-phase operation at temperatures of 500°C (932°F) or somewhat higher, and pressures of about 500 pounds per square inch. If the temperature of the process is more moderate, the content of olefins is somewhat lower, and *vice versa*. As mentioned above, the content of olefins decreases under high cracking pressures. The average data of Table 9 relate to commercial vapor-phase operation at 550° to 600°C (1022° to 1112°F) and low pressures.

Table 9. Average Chemical Composition of Cracked Gases Produced in the Vapor-phase Process.

Low-pressure condensation.

Specific Gravity (air = 1) from 1.00 to 1.10.

	% by Vol		% by Vol
Hydrogen	7	Butanes	2
Methane	30	Butenes	6
Ethane	12	Butadiene	1
Ethene	23	Higher	1
Propane	4	Total Olefins	44
Propene	14		

Table 10. Chemical Composition of Cracked Gases in Vapor-phase Cracking of Spray Oil vs. Temperature.

Temperature (°C)	600	650	700	750	800	850
Yield of gas (% by wt)	14.2	45.2	52.2	58.5	58.0	52.9
Chemical Composition (% by wt of cracking stock)						
Hydrogen	0.1	0.3	0.4	0.5	0.7	1.4
Methane	2.2	6.7	10.2	15.9	16.5	19.6
Acetylene	0.0	0.0	0.0	0.0	0.0	0.6
Ethene	4.3	13.0	16.2	21.2	24.6	23.4
Ethane	1.6	3.8	4.3	5.1	4.2	3.2
Propene	3.7	11.2	13.4	11.3	11.3	4.3
Propane	0.4	2.9	1.9	1.6	0.7	0.4
Butenes	1.7	6.4	5.3	2.9	0.0	0.0
Butanes	0.2	0.9	0.9	0.3	0.0	0.0
Total Olefins	9.7	30.6	34.9	35.4	35.9	28.3

The content of olefins in the gases of vapor-phase cracking increases with rising temperature to a maximum at about 750°-800°C (1382° to 1572°F). At still higher temperatures or for a very long duration at more moderate temperatures, the decomposition of olefins is considerable, resulting in an increasing content of hydrogen and methane at the expense of olefins. The data of Groll,²³ given in Table 10, clearly show this phenomenon. It should be noted that the figures of Table 10 are expressed in weight per cents of the charging stock and cannot be directly compared with those of the previous tables.

Table 11. Average Composition of Cracked Gases Produced in the Houdry Process.

(Low-pressure condensation)

Specific Gravity about 1.45.

Gas	% by Vol	Gas	% by Vol
Hydrogen	7	Propene	18
Methane	11	Butenes	10
Ethane	5	Heavier	5
Ethene	4	Isobutane	22
Propane	14	n-Butane	4

The composition of cracked gases from catalytic cracking (Houdry Process) is given in Table 11.

The gases from catalytic cracking contain a greater percentage of C_3 and C_4 hydrocarbons and hydrogen than do those obtained by thermal methods. The high percentage of isobutane should also be noted.

The composition of gases after thermal reforming is close to that of cracked gases obtained in the mixed-phase process, but the severe conditions of reforming make the resulting gases somewhat richer in hydrogen and unsaturates.

Cracked gases produced in modern commercial units do not contain acetylene but may contain a small proportion of butadiene, which increases with rising process temperature. Accordingly, the gases from vapor-phase cracking are richer in butadiene (up to 2 to 3 per cent). It should be pointed out that the conditions of vapor-phase cracking to yield gasoline do not coincide with the optimum conditions for producing butadiene. High temperatures [up to 750°C (1382°F)], short reaction time, and very rapid cooling of the reaction products favor butadiene formation and suppress the secondary reactions of the butadiene formed. Under these conditions, butadiene and aromatic hydrocarbons are the main products of cracking. Cooke⁸ gives the following data on the content of butadiene and other unsaturates in cracked gases from 225° - 400°C naphtha:

	High Temp—Short Time	High Temp—Long Time
Butadiene	10% b wt	6% b wt
Butenes	14% "	18% "
Propene	9% "	19% "
Ethene	23% "	21% "

The percentage is given with respect to the charging stock.

The chemical composition of cracked gases produced by aromatization of petroleum products is close to the data of Table 10 at 700° - 800°C . For instance, Dunstan and Howes¹⁹ give the following figures for the composition of cracked gases formed in aromatization of propane and butanes at 750° - 900°C (1382° - 1472°F):

Hydrogen	10-25% by vol
Methane	50-65% "
Ethene	20-25% "
Ethane	0-10% "

The gases of the Pintsch process and other processes for producing gases and aromatics from petroleum have a similar composition due to the similarity in temperature conditions. Thus Pintsch gas consists of

Hydrogen	10-20% by vol
Methane	30-40% "
Ethane	5-15% "
Olefins, mostly ethene	20-40% "

Aromatization gases contain about 2 per cent of acetylene.

The analytical data given above include only the content of hydrogen and hydrocarbons, which can be considered as normal constituents of

cracked gases. The content of "impurities," such as carbon dioxide, nitrogen, and hydrogen sulfide, usually does not exceed one to two per cent. The content of hydrogen sulfide, however, may be considerably higher, depending upon the nature and source of the charging stock; in some cracked gases high in sulfur, *e.g.*, from Mexico, Venezuela, and California stocks, it amounts to five to ten per cent.

Hydrogenation gases, after the removal of hydrogen, consist of methane hydrocarbons, including methane, ethane, propane and butanes, together with hydrogen sulfide. When charging stocks high in sulfur are hydrogenated, the content of hydrogen sulfide may be high, because of the almost complete transformation of all sulfur compounds into hydrogen sulfide in the presence of high-pressure hydrogen. Olefins are entirely absent from hydrogenation gases.

The butane-butene or B-B fraction of stabilizer gases from commercial cracking is of particular value, since this fraction contains isobutene and butenes which are widely used for the commercial synthesis of high-octane hydrocarbons. These hydrocarbons are obtained either by polymerization and subsequent hydrogenation or by alkylation.

The butane-butene fraction produced from cracked gasolines of the mixed-phase process usually contains about 50 per cent of butanes, 35 per cent of normal butene and 15 per cent of isobutene. The content of butanes in the butane-butene fraction may be higher than 50 per cent, but the ratio of normal to isobutene remains close to 2:1. The percentage of normal butane is usually somewhat greater than that of isobutane.

A typical analysis of the B-B fraction from thermal mixed-phase cracking is given in the following table:

Propane and propene	2 per cent by vol
<i>n</i> -Butane	38 " " " "
Isobutane	13 " " " "
<i>n</i> -Butenes	31 " " " "
Isobutene	15 " " " "
Heavier	1 " " " "

Snow⁴⁰ gives the following composition of the B-B fraction (mixed-phase cracking):

Isobutane	11.4 per cent by vol
<i>n</i> -Butane	49.0 " " " "
Isobutene	10.1
Butene-1	10.4
Butene-2	18.2 " "
Butadiene	0.9 " "

The B-B fraction of catalytically cracked gasolines is richer in isobutane and poorer in isobutene, as the following data indicate:

<i>n</i> -Butane	12 per cent
Isobutane	53 " "
<i>n</i> -Butenes	25 " "
Isobutene	6 " "
Lighter and heavier	4 " "

The absence of butadiene from catalytically cracked C_4 fraction should be mentioned.

A few years ago cracked gases were considered as waste products, and were used as the cheapest sort of fuel. The polymerization, alkylation and thermal conversion of hydrocarbon gases containing olefins into high-octane gasolines have increased the intrinsic value of cracked gases. Stabilizer gases, containing a large proportion of olefins, are particularly valuable as charging stocks for the processes in question. Receiver gases, low in olefins and rich in unconvertible methane and ethane, cannot be processed directly, and have to be treated with oils or solvents to increase the concentration of convertible hydrocarbons.

Refinery Gases

The gas formation on straight-run distillation of crude oils, as well as during their storage, is due to the presence of dissolved gases. The percentage of hydrocarbon gases (including C_4) in commercial light crude oils was recently determined by Askevold and Agruss²; in such crudes as Michigan, Van Zandt, and Cabin Creek, it varied from 1 to 2 per cent by weight. Ethane is present in traces, propane and isobutane in quantities from 0.1 to 0.5 per cent, and *n*-butane from 0.5 to about 1.0 per cent. Parker and Ragatz^{38a} give the following content of light hydrocarbons in a 31° A.P.I. California crude oil:

C_3 and lighter	0.35 per cent by vol
Isobutane	0.20 " " " "
<i>n</i> -Butane	0.70 " " " "
Isopentane	0.60 " " " "
<i>n</i> -Pentane	0.75 " " " "

Refinery gases, i.e., those produced in refineries as a result of various processes, are predominantly cracked gases. As a matter of fact, cracking produces the largest quantity of gas, amounting on the average to 500 cubic feet per barrel of cracking stock. Other processes and parts of refineries produce much smaller amounts. Table 12 gives some average data on the gas formation in different processes used in modern refineries.

Table 12. Gas Formation in Refineries.

Process	Cu ft per bbl of Charging Stock
Cracking (mixed-phase) (receiver)	350
Coking	200
Stabilization of pressure (distillate)	600
Straight-run distillation, 60-70% overhead	10

The composition of coking gases is similar to that of cracking, but these gases are richer in butane and heavier constituents. The composition of stabilizer gases has been given above. The gases released in straight-run distillation and during storage are very rich in heavier hydrocarbons, as the data of Table 13 clearly show.

Table 13. Average Composition of Gases from Straight-run Distillation and Storage.

Methane	5 % by vol
Ethane and ethene	10 " " "
Propane and propene	30 " " "
Butane and butenes	35 " " "
Pentanes and heavier	20 " " "

Natural Gasoline

Natural gasoline is produced from natural or casing-head gas by compression or absorption under pressure. Adsorption on carbon is used to a very limited extent in this country. As has been stated above, the yield as well as the chemical composition of natural gasoline depends upon the composition of natural gas. The condensible portion of natural gas includes butanes and heavier hydrocarbons and some propane.

Nelson³⁵ gives the following approximate data on the yield of liquefied hydrocarbons in gallons per 1,000 cubic feet of gas:

Propane	26.6
Butane	31.4
Isobutane	32.4
Pentanes	36.3
Hexanes	41.2
Hexanes and heavier (ave)	43.0

For olefins the above figures must be reduced by about 10 per cent. The yield of recoverable natural gasoline includes butanes and heavier hydrocarbons. The recovery of propane in commercial gasoline plants is only partial—not over 25 per cent of the actual amount of propane—since this hydrocarbon cannot be used in gasolines and has to be removed in stabilization.

Raw natural gasoline is too unstable with respect to evaporation and has too high a vapor pressure to be used in motors. Therefore, the raw product is stabilized or fractionated in a conventional unit to separate propane, excess isobutane and normal butane, and to produce a stabilized natural gasoline of proper vapor pressure. Raw natural gasoline differs from the stabilized product by the excess of lighter constituents, as will be seen from Tables 14 and 15. The data were obtained by Podbielniak analysis (Cody and Luntz⁷).

Thus raw natural gasoline may contain as much as 55 per cent of propane and butanes, while stabilized gasolines contain no more than 20 per cent of butane. Butane-free natural gasoline may easily be produced, if required, as shown by the data of Table 14.

The composition of a very light gasoline including a large proportion of propane is given in Table 16. Such natural gasolines of very high vapor pressure are produced under high pressures of absorption or compression. It should be mentioned that, on account of the expanding use of liquid propane and butanes, utilization of the light constituents of natural gas, *i.e.*, propane and butanes, by absorption or compression is now much greater than it was a few years ago.

Table 14. Composition of Raw and Stabilized Natural Gasolines.

	Raw	Stabilized	Debutanized
A.P.I. Gravity (60°F)	92.5	77.8	74.5
Specific Gravity (60°/60°F)	0.6309	0.6761	0.6869
Vapor Pressure (Reid) (lbs/sq inch, 100°F)	60	17.5	11.0
Ethane (% by vol)	1.5		
Propane	14.7		
Isobutane	10.2	1.5	
<i>n</i> -Butane	30.3	15.3	3.2
Isopentane	4.8	7.2	8.5
<i>n</i> -Pentane	15.0	21.0	24.5
Heavier	23.5	55.0	63.8

Table 15. Composition of East Texas Natural Gasolines (Stabilized).

	26-lb Natural	Same, Debutanized	18-lb Natural	Same, Debutanized
A.P.I. Gravity (60°F)		81.9	81.5	77.0
Specific Gravity (60°/60°F)		0.6631	0.6643	0.6787
Vapor Pressure (Reid) (lbs/sq inch, 100°F)	26	13.2	17.5	8.9
Butanes (% by vol)	33.6		16.6	
Isopentane	17.2		12.1	
<i>n</i> -Pentane	20.6		17.2	
Heavier	28.6		54.1	

Table 16. Composition of 80-pound Natural Gasoline (Texas).
mol per cent

Methane	none
Ethane	trace
Propane	38.7
Isobutane	10.0
<i>n</i> -Butane	18.3
Pentanes	20.0
Heavier	13.0

Table 17. Vapor Pressure and Butane Content of Regular and Natural Gasolines.

Reid Vapor Pressure (lbs/sq inch)	% Butanes (approximate)
8, regular 400°F.E.P.	6.6
10, regular 400°F.E.P.	10.0
12, regular 400°F.E.P.	14
14, natural (20% at 140°F)	14
18, natural (50% at 140°F)	18
22, natural (55% at 140°F)	15-24
26, natural (70% at 140°F)	24-33
30, natural (70% at 140°F)	33-42

The vapor pressure of natural as well as of regular gasolines depends largely upon the content of butanes. Nelson⁸⁸ gives a table for approximate evaluation of the butane content from the Reid vapor pressure of gasolines (Table 17).

Stabilization of natural gasolines forms stabilizer gases containing mostly propane and butanes. In addition to the use of liquid propane and butanes, as domestic fuel, stabilizer gases at the present time find other important applications, as for instance a material for thermal polymerization or a source of isobutane for alkylation. Propane and butanes decompose thermally to a much greater extent than methane and ethane, producing olefins which may be polymerized to high-octane gasolines or hydrocarbons. The separation of isobutane is performed by fractiona-

tion of stabilizer gases under appropriate conditions. The content of isobutane is of primary importance for such an operation. In stabilizer gases, as well as in natural gasoline, it is usually from one-half to one-sixth that of normal butane.

Commercial propane and butanes (bottled gases) are produced from the overhead of stabilizing units. The overhead distillate is fractionated in a special fractionating column under pressure of about 200 lbs/sq inch and separated into butanes (bottoms) and propane (overhead), which contains some ethane. If required, propane can be deethanized, or separated from ethane, in another special fractionating column under a pressure of about 400 lbs/sq inch. Commercial propane is comparatively pure and contains usually from 90 to 98 per cent propane. The Reid vapor pressure of this product at 100°F is about 200 lbs/sq inch. The impurities are ethane, isobutane and normal butane.

Commercial butane is less uniform, containing variable proportions of normal and isobutane. Normal butane usually comprises up to 70 per cent. A small proportion of propane (from 5 to 10 per cent) may be present in a commercial product. The Reid vapor pressure of commercial butane is about 60 lbs/sq inch.

The commercial production of liquid butanes and propane started about 15 years ago. The production of these liquefied gases in 1944 reached 785 million gallons, not including C_3 and C_4 hydrocarbons for alkylation, synthetic rubber, etc.,³⁷ thus the total production of such gases greatly exceeds the above figure. In addition to C_3 and C_4 hydrocarbons, isopentane also is separated from natural gas, as a high-octane and volatile constituent of aviation gasolines.

Harts²⁵ described the commercial methods of fractionation of natural gasolines for separation of isopentane and isobutane. The separation of isopentane is performed as follows. A Mid-Continent natural gasoline is fractionated in the first column, having 30 trays, under a pressure of 150 lbs/sq inch, the temperature of the top being 135°F and of the bottoms 313°F. In this column the pentanes and heavier fractions are separated from the butanes and lighter fractions, the yield of the former being about 30 per cent by volume. The pentanes, etc., are pumped to a second fractionating stage, which consists of two columns containing a total of 70 trays. These columns operate with a high reflux ratio, 22:1, at a pressure of 50 lbs/sq inch, the top temperature being 170°F and the kettle temperature 202°F. Isopentane of a purity of 93.4 per cent (mostly butane as impurity) is produced overhead and finally purified in a third column having 30 trays and operating under a pressure of 100 lbs/sq inch, with temperatures in the top and in the kettle of 162° and 216°F, respectively. In this column butane is separated from isopentane of 99 per cent purity. The yield of isopentane from mid-Continent natural gasoline is 5 per cent by volume.

The fractionation of isobutane is carried out by a similar procedure. Natural gasoline is deethanized in the first column, containing 30 plates,

under a pressure of 250 lbs/sq inch. The bottoms are pumped to the second 30-plate column under a pressure of 140 lbs sq inch (top temperature 158°F and kettle temperature 226°-271°F). In this column the overhead vapors, consisting of propane, isobutane and normal butane, are separated from heavier constituents. The condensed overhead distillates are pumped into a third 30-plate column under a pressure of 250 lbs/sq inch, the top and kettle temperatures being 124° and 227°F, respectively. This column separates propane from butanes, which then enter a fourth column under a pressure of 125 lbs/sq inch, with top and kettle temperatures of 144° and 170°F, respectively. This column contains 50 plates and operates with a reflux ratio of 17:1, whereas the others have a reflux ratio of only 6:1. The last column separates isobutane from normal hydrocarbon. The yield of isobutane from the mid-Continent natural gasolines used for producing isobutane is from 5 to 8 per cent.

A similar procedure for separation of hydrocarbons on a commercial scale was described by Foster.¹⁹

The production of liquefied propane, butanes, isobutane and isopentane is of particular interest, since only these hydrocarbons and some aromatics are manufactured on a large scale from petroleum.

There are few reliable data relating to the composition of heavier fractions of natural gasoline, *i.e.*, those containing hydrocarbons heavier than C₅, as well as cyclopentane. Anderson and Erskine² were probably the first to fractionate a natural gasoline having a specific gravity of 0.6667 (15°/15°C). They separated the natural gasoline by five fractionations into four portions corresponding to the normal paraffins present in the gasoline: pentane, hexane, heptane and octane. The portions obtained were repeatedly fractionated for separation of individual hydrocarbons. They are believed to have separated the above paraffins, as well as isopentane, 2-methylpentane and 2-methylhexane. The following approximate composition of the gasoline has been given:

Propane and butanes	20 % by vol	Isoheptane	8 % by vol
Isopentane	13 " " "	<i>n</i> -Heptane	12 " " "
<i>n</i> -Pentane	17 " " "	Octanes	4 " " "
Isohexane	9 " " "	Absorption oil	2 " " "
<i>n</i> -Hexane	15 " " "		

It should be emphasized, however, that the separation was rough and insufficient, as is clearly shown by the specific gravities of the hydrocarbons isolated. With the exception of isopentane and normal pentane, their specific gravities are invariably much higher than those of the individual paraffins, indicating that the hydrocarbons separated contained an appreciable proportion of naphthenes, as might be expected. The foregoing data are apparently fairly correct with respect to the content of low molecular weight paraffins, including pentanes.

Ayres³ found neopentane in natural gasolines of West Virginia and Texas to the extent of 2 per cent.

Bruun, Hicks-Bruun and Faulconer⁴ fractionated a cut of natural gasoline from the Clendendin Gas Field (West Virginia) in a 100-plate column and isolated the following hydrocarbons in a pure state:

	in Cut °-65°C	Amount in Natural Gas (cc/m ³)
2,3-Dimethylbutane	8	74
2-Methylpentane	45	420
3-Methylpentane	21	196

The same authors⁵ isolated 2,2-dimethylbutane (neohexane) from the same natural gas. This hydrocarbon is present in natural gas in the amount of 168 cc/m³.

Griswold, Van Berg and Kasch²² recently studied a commercial C₆ fraction, or Skellysolve B (74.9° A.P.I. gravity, boiling range from 148° to 165°F), produced from Burbank natural gasoline. The following hydrocarbons were separated from this fraction:

	Per Cent by Volume
<i>n</i> -Pentane	1.2
Cyclopentane	0.2
2,3-Dimethylbutane	2.4
2-Methylpentane	16.0
<i>n</i> -Hexane	58.8
Methylcyclopentane	16.4
Benzene	1.8
Cyclohexane	3.2

Tooke⁵³ determined the percentage of cyclopentane in the same natural gasoline (Burbank, Oklahoma). The natural gasoline, stabilized to 12 lbs pressure, was fractionated, and the C₅-C₆ fraction (boiling range

Table 16b. Hydrocarbons Separated from Natural Gasolines.

Hydrocarbon	Per Cent
Ethane	very small in raw gasolines; none in stabilized
Propane	3 to 25 in raw gasolines; none in stabilized
Isobutane	5 to 15 in raw gasolines; 0 to 5 in stabilized
<i>n</i> -Butane	30 to 40 in raw gasolines; 15 to 25 in stabilized
Neopentane	up to 2 per cent in some gasolines
Isopentane	10 to 25 in stabilized
<i>n</i> -Pentane	10 to 25 in stabilized
2,2-Dimethylbutane	up to 10 in stabilized
2,3-Dimethylbutane	
2-Methylpentane	
3-Methylpentane	
<i>n</i> -Hexane	up to 30 in stabilized
<i>n</i> -Heptane and isomers	up to 40 in stabilized
<i>n</i> -Octane and isomers	
Cyclopentane	up to 2-3 in some stabilized
Methylcyclopentane	up to 3 in stabilized
Cyclohexane	1 or more in stabilized
Benzene	less than 1 in stabilized

from 88° to 210°F) was separated. The cyclopentane content in this fraction was 5.7 per cent by volume and in the total gasoline 2.4 per cent.

Boulbee⁵⁴ gives the most complete data on the chemical composition of a California unstabilized natural gasoline (Table 16c). The propor-

tion of isoparaffins and naphthenes in this natural gasoline is much greater than in those from Mid-Continent. On the contrary, the content of normal paraffins seems to be unusually low. As will be seen in Chapter 3, some straight-run California gasolines also are rich in isoparaffins and naphthenes and poor in normal paraffins.

Table 16c. Hydrocarbons in California Natural Gasoline.

Hydrocarbon	Per Cent by Volume
Methane and ethane	0.5
Propane	7.5
Isobutane	8.5
<i>n</i> -Butane	28.8
Isopentane	11.3
<i>n</i> -Pentane	9.9
Cyclopentane	0.9
Isohexanes	7.5
<i>n</i> -Hexane	3.9
Methylcyclopentane	2.4
Benzene	0.7
Cyclohexane	1.1
Dimethylcyclopentanes	3.0
Isoheptanes	3.2
<i>n</i> -Heptane and isooctanes	1.6
Methylcyclohexane	1.5
Toluene	0.7
<i>n</i> -Octane and heavier	7.0
	100.0

Thus the presence of cyclic and aromatic hydrocarbons in natural gasolines is beyond doubt. The paraffins, however, greatly predominate in stabilized natural gasolines, probably amounting on an average to 80 per cent. The old determinations of aromatics in a Pennsylvania natural gasoline by Erskine,¹⁸ 2.4 per cent *in toto*, are apparently erroneous and were caused by the errors of the method of nitrobenzene points used by the author. The hydrocarbons found and isolated in natural gasolines are summarized in Table 16b.

The so-called "condensate" produced from distillate wells⁴⁵ has the properties and composition of natural gasoline but contains a much smaller proportion of light hydrocarbons, *i.e.*, propane and butanes. Sage and Lacey⁴⁶ give the following composition for a Kettleman Hills condensate:

% by weight		% by weight	
CH ₄	1.93	<i>n</i> -C ₄ H ₁₀	4.64
C ₂ H ₆	2.21	<i>i</i> -C ₄ H ₁₀	3.32
C ₃ H ₈	2.82	<i>n</i> -C ₅ H ₁₂	3.72
<i>i</i> -C ₄ H ₁₀	1.56		

The residuum (sp gr 0.746) had a boiling range from 128 to 441°F (A.S.T.M. distillation). As the specific gravity of narrow fractions of the residuum is appreciably higher than that of paraffins, the presence of naphthenes and perhaps of aromatics is unquestionable. The total average percentage of paraffin hydrocarbons in condensates is about 70.

Refinery Gas Gasoline

Absorption gasolines from cracked gases differ from natural gasoline by the presence of unsaturated hydrocarbons which may amount to 40 per cent of the total. Tannich, Thomas and Padgett⁵² fractionated a "plant-stabilized naphtha" [butane-free; 79.6 A.P.I. gravity; boiling range from 90° to 273°F (95%)] and determined the percentage of unsaturates in the narrow fractions by the iodine-thiocyanate method. The results are given in Table 17.

Table 17.

Fraction	Temperature Range (°F)	% by Volume
Isopentane	70-85	15.5
Pentenenes	" "	6.4
Normal pentane	85-100	24.4
Pentenenes	" "	11.5
Saturates (Cyclopentane fraction)	100-130	1.6
Unsaturates	" "	1.6
Saturates (Isohexane fraction)	130-150	5.3
Unsaturates	" "	2.0
Saturates (<i>n</i> -hexane fraction)	150-160	6.1
Unsaturates	" "	1.7
Saturates (Isoheptane Fraction)	160-200	7.6
Unsaturates	" "	1.8
Saturates (<i>n</i> -heptane Fraction)	200-215	3.9
Unsaturates	" "	0.7
Saturates (Residuum)*	215-up	8.4
Unsaturates*	" "	1.5

*Calculated from the total percentage of the fraction (9.9 per cent), assuming that the relative proportion of unsaturates is 15 per cent.

The total percentage of unsaturated hydrocarbons in the gasoline is 27.2; that of pentanes and pentenes (fractions boiling up to 100°F) is very high, amounting to 58 per cent.

The non-hydrocarbon constituents of natural and refinery gasolines, *i.e.*, mostly mercaptans and some oxygen compounds, will be discussed in Chapters 7 and 8.

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Chapter 2

Physical Methods of Determining Hydrocarbons in Distillates

The physical methods for determining the chemical composition of petroleum may be divided into two main groups. To the first group belong such methods as distillation, crystallization, solvent treatment, and adsorption, by which individual hydrocarbons or hydrocarbon classes are actually separated according to their properties: boiling point, melting point, solubility, or adsorption characteristics.

To the second group belong other methods in which no actual separation takes place; the determination of hydrocarbons (or hydrocarbon classes) is carried out on the basis of a certain physical property, which is either a linear function of the composition (specific gravity, refractive index, aniline point, etc.) or is determinable for each constituent independently of the others (infrared, ultraviolet, Raman, mass spectra, etc.).

Thus, only physical properties, which are well known for various hydrocarbons and hydrocarbon classes, can be used for determining the chemical composition of petroleum. Such properties as fluorescence and optical activity are almost useless from this standpoint, since the substances causing them are entirely unknown. The color of petroleum products depends upon the content of neutral resins and asphaltenes, but the optical properties of these asphaltic constituents have not been studied. Viscosity is a property easily determinable for any fraction and is well known for various hydrocarbons, but the viscosity method seems to be of little value for the determination of the composition of fractions, since there is no linear relationship between the viscosity of mixtures and their composition. All these considerations limit the application of physical methods to the problem in question.

The physical methods which are in wide use for separation and quantitative determination of individual hydrocarbons or hydrocarbon classes in petroleum may be classified by:

- (1) Distillation
 - (a) at atmospheric pressure
 - (b) at pressure other than atmospheric
 - (c) azeotropic
 - (d) in molecular stills
- (2) Crystallization
 - (a) simple
 - (b) in appropriate solvents

- (3) Adsorption and desorption
- (4) Solvent treatment
- (5) Critical solubility temperatures
- (6) Specific gravity and refractive index
- (7) Refractive intercept and specific dispersion
- (8) Methods based on other physical properties of hydrocarbon mixtures
- (9) Infrared and ultraviolet spectra and Raman effect
- (10) Mass spectrometry
- (11) X-rays

The methods of fractional distillation and crystallization are the most important and most generally used; they give a very effective separation of individual hydrocarbons. Other physical and chemical methods to be described in the following chapters can be successfully used only in conjunction with these two basic methods of separation.

The use of infrared and Raman spectra and mass spectrometry gives very promising results for narrow fractions containing a limited number of hydrocarbons. If the narrow fraction consists of hydrocarbons of the same class, *e.g.*, of paraffins or naphthenes, these methods excel all others for purposes of identification and quantitative determination. On the other hand, the application of such methods to large fractions containing a great number of individual constituents is made practically impossible by the superimposition of absorption bands or lines. Thus, it should be expected that the combination of very efficient fractionation (particularly by distillation) with infrared and Raman spectra and mass spectrometry will conspicuously contribute to the knowledge of the chemical composition of petroleum.

Distillation

The progress in laboratory and commercial equipment for fractional distillation in the last ten years has been stupendous. A few years ago, the quantitative separation by fractionation of two hydrocarbons with a difference in boiling point of about 10°C was hardly possible, unless very large charges and numerous distillations were employed. The modern efficient laboratory columns separate in one fractionation two hydrocarbons differing in boiling point by only 2° or 3°C. This progress has made possible the separation of numerous individual hydrocarbons boiling in the range of gasolines and kerosenes.

The fractional distillation of some petroleum cuts in many cases produces hydrocarbons of high purity, more than 95 mole per cent—a result which seemed impossible only a few years ago. The progress in commercial fractionation is no less significant. Ten years ago, separation of gasoline from kerosene, as well as of other commercial fractions, with “gaps” in Engler distillation between the end point of the lighter fraction and the initial boiling point of the heavier fraction was considered as the maximum effect of commercial distillation. Now the separation of such

hydrocarbons as isobutane, normal butane, isopentane, and toluene is carried out on a commercial scale. If required, various other hydrocarbons, particularly normal paraffins in Pennsylvania or some Mid-Continent gasolines, can be separated commercially with a high degree of purity.

The fact that no typical azeotropic mixtures exist between various hydrocarbons facilitates wide application of fractional distillation for separating petroleum hydrocarbons in laboratory and commercial practice. Theoretically, any non-azeotropic mixture of hydrocarbons can be resolved into individual hydrocarbons in a column with an appropriate number of plates, provided that the boiling points of the hydrocarbons to be separated are not identical. Even if such is the case, fractionation under varied pressures will perform this separation, since the boiling points, identical under atmospheric pressure, will be different under a higher or lower pressure.

It should be understood that the fractionation and separation of petroleum into individual hydrocarbons, or into very narrow fractions containing a small number of individual hydrocarbons, is impossible in one operation. The first fractionation is usually conducted on a large scale in a column with a comparatively moderate number of plates (*e.g.*, about 30) and serves only to separate a number of relatively large cuts. The cuts produced or their appropriate combinations are fractionated with smaller, but more efficient columns to obtain narrower cuts, which may be repeatedly refractionated with columns of high separating power. The separation of hydrocarbons which are present in petroleum products in small proportions is a very difficult problem, and requires many consecutive fractionations. As will be seen later, simple fractionation is frequently combined with solvent treatment, azeotropic distillation, fractional crystallization and chemical methods.

Distillation can be performed under atmospheric pressure, elevated pressure, or in a vacuum. It is recommended that fractionation be performed in the absence of air, *i.e.*, in an atmosphere of nitrogen or carbon dioxide, particularly at higher temperatures. In this way the oxidizing effect of air is completely eliminated.¹²⁹

There is a considerable difference in the design and construction of commercial and laboratory columns due partly to the much smaller size of the latter and partly to the great number of constituents to be separated in them. Whereas only one or two individual hydrocarbons or fractions are obtained in commercial fractionation, the ultimate purpose of laboratory fractionation is to separate a product more or less completely into its individual constituents.

The commercial bubble-type fractionating column is not largely used in laboratory practice due to their great height. As will be seen later, however, very efficient small columns of this type have been developed recently. On the contrary, packed columns are used extensively, particularly for small throughputs. The channelling effect, which prevents wide

commercial use of packed columns, is insignificant in laboratory columns if a small diameter, particularly in those provided with small-size packing elements. The effectiveness of packed columns may be very high and the height equivalent to a theoretical plate may be very small, provided the channelling effect is eliminated. In contradistinction to commercial columns, the operation of laboratory columns is mostly discontinuous (batch operation). As a result, the initial charge is split into several individual hydrocarbons or narrow cuts comprising a minimum number of individual hydrocarbons.

The separation of pure hydrocarbons, or at least of narrow fractions containing an excess of an individual hydrocarbon, by fractionation in modern efficient columns is so far feasible only for liquefied gases, gasolines and kerosenes. No individual hydrocarbons could be separated from higher-boiling fractions either by fractionation or by any other known method.

Even very narrow lubricating fractions separated in the Bureau of Standards by fractional distillation (and solvent treatment), representing only 0.0025 per cent of the original crude oil, are not individual hydrocarbons; however, they approach individuals more closely than any material hitherto separated from lubricating fractions.

Number of Theoretical Plates

The separating power of a fractionating column depends upon the number of theoretical plates on which the equilibrium between vapor and liquid is effected. For bubble-type towers this number equals the number of actual plates multiplied by the plate efficiency. The plate efficiency of commercial columns ranges from 50 to 90 per cent; that of laboratory columns is closer to the upper limit, ranging from 70 to 90 per cent of theoretical. For packed columns, the number of theoretical plates equals the height of the packed space divided by the height equivalent to a theoretical plate (or H.E.T.P.). Thus the H.E.T.P. is the most important characteristic of packed columns, predetermining their separating power as well as their height.

The number of theoretical plates required for fractionation of a mixture of two individual compounds can be calculated either graphically or algebraically. A comprehensive review of these methods was given recently by Ward.¹²⁰ The calculations in question are valid for "ideal" mixtures, *i.e.*, those obeying Raoult's law, which is the case for hydrocarbon mixtures. The calculation is simplified for the total reflux conditions under which all the vapors are condensed and returned to the column, and thus no distillate is withdrawn from the column.

Only simple equations for the calculation of the number of theoretical plates with total reflux are discussed in this chapter. If x_1 and x_2 are the molar fractions of the first and second components respectively in the still, y_1 and y_2 are those of the first and second components in the distillate, and α is the ratio of the vapor pressure of the two components, then

the number of theoretical plates, n , in the column (continuous operation) is calculated, according to Fenske,³⁷ by the equation:

$$n = \frac{\log \frac{y_1}{y_2} - \log \frac{x_1}{x_2}}{\log \alpha} - 1$$

The calculation by Fenske's formula requires the knowledge or determination of α . Ewell* developed a formula in which α is replaced by the boiling temperatures of the components:

$$n = \frac{T_2 + T_1}{21(T_2 - T_1)} \log \text{nat} \frac{\left(\frac{1}{y} - 1\right)}{\left(\frac{1}{x} - 1\right)}$$

In this equation 21 represents the Trouton constant; T_2 the condensing temperature in column head (or that of a more volatile component); T_1 the vapor temperature in still pot (or that of a less volatile component); x and y the mole fractions of a more volatile component in still and distillate respectively.

Rose³⁹ gives a simplified equation for a "standard" batch separation, in which the first 40 per cent distilled over will have an average purity of the more volatile component of greater than 95 per cent. The mixture to be fractionated consists of 50 mole per cent of each component. Thus, according to Rose:

$$n_{\text{(optimum)}} = \frac{2.85}{\log \alpha}$$

or

$$n_{\text{(optimum)}} = \frac{T_1 + T_2}{3(T_2 - T_1)}$$

The reflux ratio is numerically equal to n . Calculation on the basis of the last equation shows, for instance, that the separation of two hydrocarbons (95 per cent purity of a more volatile component in the first 40 per cent distilled), boiling at 100° and 102°C respectively, from a mixture containing 50 mole per cent of each component is feasible with a column having 125 theoretical plates. As will be seen later, the construction and operation of such columns in an average laboratory does not present any practical difficulties.

According to Fenske *et al.*,⁴¹ "by using columns with seventy-five to one hundred plates, it is possible to separate petroleum either into extremely narrow-boiling fractions or else into practically pure hydrocarbons."

* Private communication.

Unpacked Columns

The use of fairly efficient unpacked (empty) columns seems inconsistent with ceaseless efforts to develop more efficient packings. It should be kept in mind that the wall of the column *per se* is a sort of packing. If the diameter of the column is very small, *e.g.*, from 3 to 6 mm, the relative surface of the wall becomes comparatively large and is sufficient for intimate contact between liquid and vapor. As a result, such columns may be efficient without any packing, with certain limitations.

Rose⁹⁸ studied empty glass columns 3 and 6 mm in diameter and 30.3 cm high (carbon tetrachloride-benzene). With a very high reflux ratio of 70:1, the columns had a high efficiency at very low rates of boiling, so that the throughput was very small. For instance, the 30.3-cm column, 6 mm in diameter, was equivalent to 17.5 theoretical plates (H.E.T.P. = 1.7 cm) at a liquid velocity of 0.56 cc per minute. The efficiency of these columns, however, drops off very rapidly as the rate of distillation increases. Craig²⁶ used a glass column 7 mm in diameter, provided with a closed inner tube 4 mm in diameter, which gave an extension of the surface. The H.E.T.P. was 1.2 cm, also for very low capacities.

Selker, Burk and Lankelma¹¹¹ developed a column of the same type using closely fitting, multiple concentric glass tubes. The inner, closed tube is 4 mm in diameter; the second, outer tube is 8 mm in outside and 6 mm in inside diameter; the third tube is 12 and 10 mm in outside and inside diameter, respectively; and the fourth tube is 16 and 14 mm in outside and inside diameter, respectively. Thus annular distances of 2 mm are provided for the passage of vapor. The length of the column is 150 cm. The column is equivalent to 85 theoretical plates (H.E.T.P. = 1.8 cm) at the reflux rate of 100 cc per hour. Such columns can be successfully used for fractionation of charges of about 50 cc. It is understood that the hold-up of these columns is very small, being equal for the above specific example to about 5 cc. The back-pressure is also very small, not exceeding 0.4 mm of mercury.

The theory of unpacked columns developed by Westhaver¹³⁰ shows that the H.E.T.P. of such columns largely depends upon the diameter and vapor velocity. At a diameter equal to or less than 5 mm and at vapor velocities less than 10 cc/sec, the H.E.T.P. may be less than 5 cm.

Thus the empty columns are comparatively efficient, except that the diameter of the column is very narrow and the capacity is small. Columns of larger diameter, having a bundle of parallel narrow tubes, may be used for greater capacities.

Bubble-type Fractionating Columns

As has been mentioned above, a wide use of laboratory bubble-type fractionating columns was considered impracticable. For instance, Fenske *et al.*³⁰ estimated the height of a plate section with a 70 per cent plate efficiency as 5 or 6 inches. Thus, the H.E.T.P. would be about 7 to

9 inches, and the total height of a column with 100 theoretical plates would be 67 feet, not including the reflux chamber.

Later investigations of the Bureau of Standards showed that the height of laboratory bubble-type columns may be rather moderate, if the proper vapor velocities are used. Bruun and Schicktzan¹⁹ described such columns made of glass, which were used by the Bureau of Standards. Each plate is provided with a single bubble cap. The plate efficiency is 87 per cent of a theoretical plate. The size and other data pertaining to such columns of three different capacities are summarized as follows:

Distillation Rate (cc/min)	Reflux Ratio	Diameter, I.D. (mm)	Height of Section (mm)	Hold-up of Each Section (cc)	H.E.T.P. (cm)
2	10:1	25	80	5	9.1
1	10:1	18	70	4	8.0
0.1-0.2	10:1	10	40	0.6	4.6

As can be seen from these data, the comparatively great value of H.E.T.P., which necessitates the construction of tall columns, and the large hold-up are disadvantages of such columns.

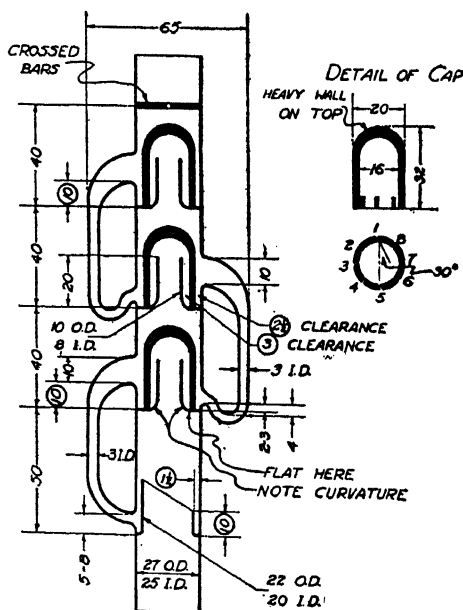


FIGURE 2. Laboratory bubble-cap glass column. (Courtesy Industrial and Engineering Chemistry)

Schicktzan¹⁰⁹ found that the plate efficiency can be increased to the theoretical (more than 98 per cent), if the bubble plates are replaced with fritted glass plates, which increase the surface of contact between vapor and liquid.

Bruun¹⁶ and Bruun and Faulconer¹⁷ described bubble-type laboratory columns also made of glass, which are more compact than those just mentioned. Each plate also has a single bubble-cap, as shown in Fig. 2. The

diameter of the two columns described was 25 mm, and the heights of each section were 20 and 40 mm, respectively. The hold-up of liquid per section was 0.7 and 1.4 cc and the pressure drop 5 and 10 mm, respectively. The columns may be used for vapor velocities up to 31.3 and 65 cm per second, respectively. A 100-plate column of this type is only about 2 meters high and can be placed in any laboratory. The number of theoretical plates in this column is between 70 and 72. Thus the H.E.T.P. for these new bubble-type columns does not exceed 2-4 cm, *i.e.*, it is of the same magnitude as for the best packed columns.

Perforated plate columns are a modification of the bubble-type columns in which the bubble caps are replaced by perforations. A column described by Oldershaw⁴⁷ consists of a series of perforated glass plates sealed into a glass column. The diameter of the column and the plate spacing are both 25 mm. Each plate has two annular rows of perforations, 22 perforations in the outer row and 20 in the inner row. In addition to this, each plate is provided with a baffle to direct the flow of liquid, a weir to maintain the liquid level, and a drain pipe. The plate efficiency, depending upon the rate of distillation, is greater for perforations of a smaller diameter. At the same distillation rate, the plate efficiency varies from 68 to 90 per cent for 1.35- to 0.65-mm perforations, respectively (benzene-carbon tetrachloride). The H.E.T.P. is low—from 0.98 to 1.47 inches. The hold-up is small, and the pressure drop is somewhat higher than in a packed column.

Packed Columns

As previously mentioned, packed columns are widely used in laboratory practice. The type of packing, which provides intimate contact of vapor and liquid, is the most important factor, as it predetermines the H.E.T.P. value. Various types of packing are used in laboratory practice, including solid packing, Raschig rings, chain packing, helices, spiral, conical wire gauze, and spiral screen.

Solid packing, such as beads or lumps of stone, glass, metal etc., is not used in efficient columns because of its relatively small surface. The effectiveness of solid packing is greatly increased by using lumps of inert, porous substances which have a much larger surface area than non-porous materials. Farnham⁴⁸ found that silicon carbide chips, or glass beads coated with such porous materials as silicon carbide or hematite, gave a better separation of two components by fractionation than did plain glass beads. Hall and Bachman⁴⁹ also showed that 3 to 6-mesh silicon carbide is much more effective than cracked glass. For instance, the H.E.T.P. for silicon carbide packing was 7.6 cm and for cracked glass packing 20.9 cm (benzene-ethene chloride). According to the same authors, silicon carbide packing compares favorably with 0.23-cm steel, single-turn helices, which are one of the most efficient column packings.

Raschig rings, *i.e.*, glass or metal tubes of approximately equal length and diameter, provide a comparatively moderate surface area unless the

size of the rings is very small. Evans *et al.*³⁵ described a laboratory column packed with glass Raschig rings 3.2 mm in diameter and 4.8 to 6.4 mm long. The H.E.T.P. in vacuum fractionation and with moderate reflux ratio was 12.7 cm. The preparation of very small Raschig rings encounters certain practical difficulties; as a result, helices and similar packing are preferred.

Chain packing may be efficient, if it is uniformly distributed throughout the column. Otherwise, the channelling effect may upset the fractionation. Jack-chain, double jack-chain and jeweler's brass locket chain were used as packing. According to Schickltanz,¹⁰⁸ the efficiency of chain packing increases from the 22 jack-chain to the 24 double jack-chain and to 13-18 locket chain, *i.e.*, with increasing surface area. A column with chain packing 2.5 cm in diameter and 250 cm long was much more effective than a 30-plate column under the same conditions of distillation rate and reflux ratio.

Multi- and single-turn helices made of wire or glass have been developed by Fenske and co-workers.^{39, 41, 122, 123} Single-turn helices give better results than multi-turn. The helices are made in sizes from 3.2 to 6.4 mm I.D., of 26-gage wire or in size 2.4 mm I.D. of 30-gage wire. The efficiency of the packing increases and the throughput decreases as the diameter becomes smaller. Single-turn helices are one of the most efficient types of packing. The H.E.T.P. of a column packed with single-turn helices may be as low as 4 cm or less for 2.4-mm helices (normal hexane-methyl cyclohexane, total reflux). As a result, laboratory columns equivalent to 100 theoretical plates packed with helices can be installed in the average laboratory. The H.E.T.P. of such columns packed with 3-mm helices is about 12 cm.

Carding teeth of appropriate size ($5\frac{1}{32}$ — $7\frac{1}{32}$ ") seem to be as efficient as single-turn helices.^{40, 123}

Spiral packing was first introduced by Podbielniak for the low-temperature fractionation of liquefied hydrocarbon gases. The wire spiral with six to eight turns to an inch, placed on the inner wall of the column, serves to distribute the reflux evenly over the column as a very thin capillary film. However, satisfactory results in the fractionation of liquefied hydrocarbons with spiral packing are due much more to great spreads in the boiling temperatures of low molecular weight hydrocarbons than to the efficiency of the packing. Columns with spiral packing give only moderate separation for fractions composed of closely boiling hydrocarbons. McMillan⁸² found that only a part of the ascending vapors follows the path between the turns of the spiral, and that another part channels straight through the center of the column without fractionation. This channelling effect can be eliminated, for instance, by inserting a central rod with a separate spiral on it or by other, similar means.

Midgley⁸⁴ increased the efficiency of columns with spiral packing by using packing coated with silicon carbide.

Conical wire-gauze packing has been developed by Stedman.¹¹³ Finc-

mesh, stainless-steel wire gauze (40-60 meshes per inch) is trimmed into flat, conical discs. Each disc is provided with a semi-circular hole on one side. The discs are welded together and form a series of sections or cells, the holes being located alternately on opposite sides of each cell (Fig. 3). Bragg¹² reported on the operation of a 61-cm (packed section) column with Stedman packing for benzene-ethene chloride mixture and total reflux. The H.E.T.P. was as low as 1.1 to 2.5 cm. Whitmore *et al.*^{142a} also confirmed that the H.E.T.P. of the Stedman columns may be as low as 1 to 2 cm.

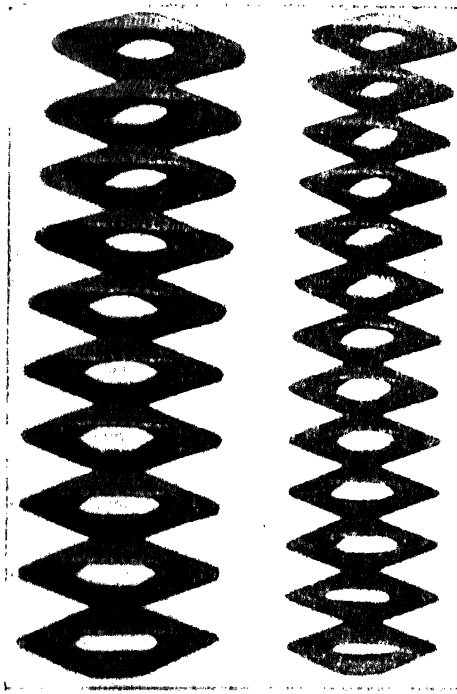


FIGURE 3. Three sizes of Stedman packing, conical type.
(Courtesy Industrial and Engineering Chemistry)

Spiral screen packing described by Lecky and Ewell⁶⁴ seems to be as efficient as conical wire-gauze packing. The screen spiral made of 60-60 or 80-80 mesh nickel gauze, is inserted closely between the inner wall of the column and the central glass tube or nickel rod. The space between the packing and the wall of the column must be tightly sealed. A 90-cm packed section of the column equivalent to from 40 to 50 theoretical plates has about 200 turns. The H.E.T.P. is about 1.7 cm.

Bower and Pray¹¹ describe an efficient gauze packing for operation when small quantities are to be fractionated.

As mentioned in Chapter 1, Podbielniak's new columns⁶⁰ have the so-called Heli-Grid packing consisting, in one modification, of wire-cage

stair-cases wound around a solid core and around each other in concentric telescopic layers (Figs. 4 and 5). The diameter of the wire is usually of

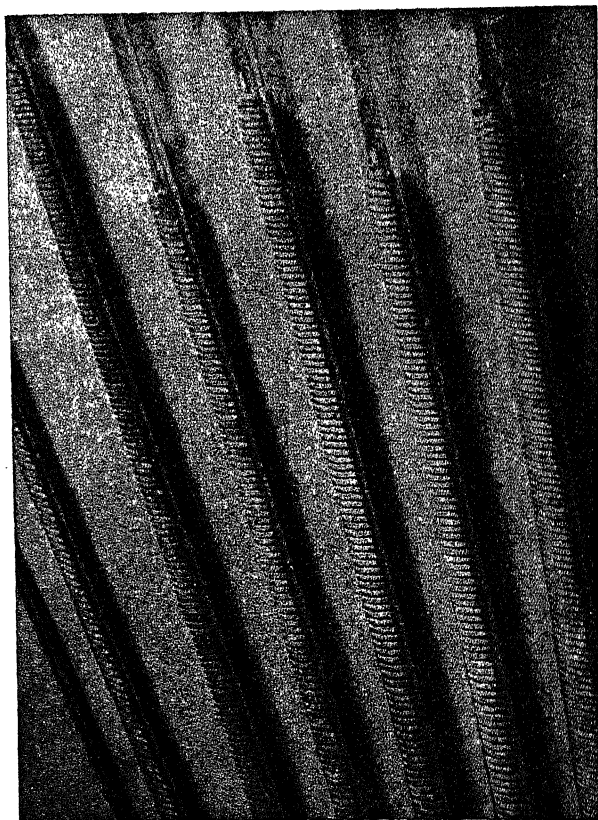


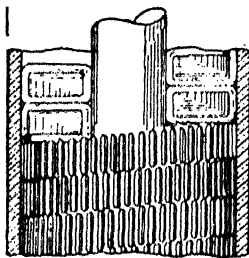
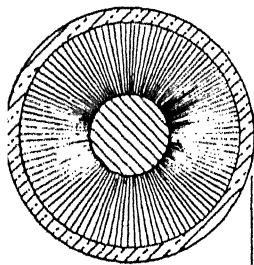
FIGURE 4. Heli-Grid packings. (Courtesy *Industrial and Engineering Chemistry*)

the order of 0.25 mm, with about the same amount of space between wires. According to Podbielniak, the packing acts like a metallic sponge absorbing and properly distributing any liquid reflux seeking to channel. The H.E.T.P. of the Heli-Grid packing is claimed to be 0.5 cm (*n*-heptane-cyclopentane, total reflux). The analytical Podbielniak columns, 85 cm high, correspond to at least 50 theoretical plates. Bower and Cooke^{10a} compared the efficiency of Stedman, Ewell and Heli-Grid columns.

The Stedman and Heli-Grid packings are used by Rossini *et al.*¹⁰⁵ in columns for separating gasolines into individual hydrocarbons. One column is adapted to fractionation of aromatics. The charge in the still of this column is 600 cc; the length and diameter 1,830 and 10 mm, respectively; the reflux ratio used is 150:1; and the rate of removal of liquid distillate is 1 cc per hour. The second column is adapted to fractionation

of paraffins and naphthenes. The charge in the still of this column is 3,600 cc. The length and diameter of this column are 1,830 and 15 mm respectively; the reflux ratio is 150:1; and the rate of removal of liquid distillate is 2-2½ cc per hour. Both columns correspond to 120 theoretical plates. Thus, the construction and use of packed fractionating columns with as many as 100 to 200 theoretical plates is quite feasible in any laboratory.

FIGURE 5. Heli-Grid packing. Staircase assembly of rectangular section coils around central core. (Courtesy Industrial and Engineering Chemistry)



Centrifugal Columns

In the columns described above, the force of gravity brings about contact between the ascending vapors and the descending liquid, as well as separation of the vapor and liquid. There is another type of column, in which the centrifugal force is used for a more intimate contact and a more complete separation of the vapor and liquid. That described by Huffman and Urey⁵⁷ is constructed as shown in Fig. 6. The column contains a series of alternate rotary and stationary metal cones. The rotary cones are connected with a shaft, the number of rotations being up to 790 per minute. Reflux from the condenser flows down a fixed cone by gravity, falls to the next rotary cone at the connection with the shaft, runs up the rotating cone by centrifugal force, and is thrown off to the wall and to the next fixed cone, etc. With this column a considerable increase in the concentration of the oxygen isotope of atomic weight 18 has been effected.

Lesesne and Lochte⁶⁵ constructed a small column of this type, in which the H.E.T.P. equals 1 inch with a total reflux. The number of revolutions is 1,000 per minute.

Mair and Willingham⁷⁹ studied centrifugal distillation columns and confirmed their high separating efficiency. Centrifugal laboratory columns with an efficiency equivalent to 200 to 250 theoretical plates can be installed in a room of ordinary height.

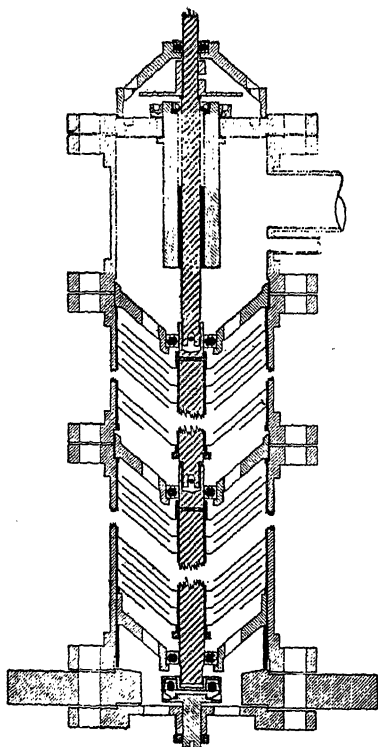


FIGURE 6. Centrifugal fractionating column. (Courtesy *Industrial and Engineering Chemistry*)

The body of laboratory fractionating columns can be made of any suitable metal, or of glass. Glass columns, provided with glass jackets, have the advantage of easy observation of the process of fractionation; for instance, overflowing can be easily detected. Glass columns of small sizes are preferred to any other columns of corresponding sizes. If the fractionating column is comparatively high, the column and packing are divided into a number of sections to prevent compression of the lower layers of the packing.

The packing, as well as the plates and bubble caps, should be resistant to corrosion, which is caused mainly by the sulfur compounds present in petroleum products. Glass, ceramic, or stainless steel packing or plates completely eliminate corrosion.

Adiabaticity of Fractionating Columns

The operation of fractionating columns is adiabatic. The heat input takes place in the still and the heat removal in the reflux chamber of the column. The temperature changes gradually from one plate or section to another, corresponding to the equilibrium conditions between liquid and vapor, which gradually change from the bottom to the top of the column. Any loss of heat by the wall of the column due to radiation or convection is a disturbing factor which produces a liquid of different composition from the equilibrium composition corresponding to a given plate or section. Thus the adiabaticity of the column should be insured by proper insulation.

Insulation with asbestos, magnesia or asbestos-magnesia is efficient and commonly used, particularly for large, tall columns. Its thickness should be at least 3 inches. Silvered vacuum jackets are also effective, and are used for small columns. Air-jackets are much less efficient, and can be used only in combination with the heating wire described below.

If the mean temperature of the column is not very far from room temperature, ordinary insulation may be sufficient to prevent an appreciable loss of heat. Usually, however, fractionation takes place at much higher temperatures; in such cases the column is provided with controlled heating effected by resistance wire or ribbon; other means of heating are used less frequently. The wrapped wire or ribbon is wound around the column in the insulation and heated to a desired temperature controlled by rheostat. Because of the gradual decrease in temperature of the column from the bottom to the top, the wire is divided into a number of sections (from 2 to 4 or more). The temperature of each section is controlled independently of the others. The temperature of any section should be approximately equal to the mean temperature of the corresponding section of the column.

In batch operation the temperature in the still and in the column gradually increases as the distillation progresses; the temperature of the insulation is gradually increased correspondingly.

Reflux

The top of the column is connected with a reflux chamber, where condensation takes place by appropriate cooling; or the reflux chamber may be arranged in the top of the column. The condenser, which is usually cooled by water (or by any other liquid in appropriate cases, including liquid air or nitrogen), may be partial or total. Total condensers are most generally employed in modern fractionating columns. There is no reason to use partial condensers, since fractionation takes place and can be controlled only in the fractionating column. Total condensation of vapors outside the column and pumping the reflux to the top of the column are usually not used in laboratory practice to a large extent.

The reflux ratio, or the ratio of the quantity of reflux to that of distilled product, is an important factor in fractional distillation. Theoretically, the greater the reflux ratio, the greater the separating power of the column. Thus the separating power of a given column is maximum at total reflux, *i.e.*, at the infinite reflux ratio. These general statements are true, provided the column is not overloaded. If such is the case, the normal operation of the column is disrupted, and the vapors channel through the flooded space without proper fractionation. As a result, the separating power of the column decreases. Flooding can be directly observed in glass columns. In metal columns it is detected by a manometer measuring the pressure in the still. The back-pressure, corresponding to the normal conditions of fractionation, appreciably increases as soon as flooding starts. It can easily be eliminated by proper control of the rate of distillation and reflux.

The values of the reflux ratio used for separation of closely boiling hydrocarbons in modern efficient laboratory columns are from 20 to 150. Efficient commercial columns for separating individual hydrocarbons, for instance, isobutane from normal butane, also have very high reflux ratios, approximately of the same order, as has been disclosed in Chapter 1, pages 34-35.

Fractionation can be performed with either constant or changing reflux ratio. Constant reflux ratio is used more frequently. Gradually increasing reflux ratio is more widely used in the case of fractionation of very large cuts, in which the first fractions are composed of a comparatively limited number of individuals, the separation of which may be performed with a lower reflux ratio, than that of high-boiling fractions composed of numerous hydrocarbons. In partial condensers the reflux ratio is controlled by varying the rate of cooling, and in total condensers by partitioning the condensate formed between the column and the final cooler. Various automatic devices are in use to keep the reflux ratio constant.

The total amount of condensate, as well as the value of reflux ratio can be calculated on the basis of the rate of water for condensation, the increase in temperature after cooling, and the latent heat of vaporization of hydrocarbons.

The pressure drop in fractionating columns depends on the design of the column and on operating conditions. Under the same operating conditions, the pressure drop in bubble-type columns is greater than in packed columns. Fractionating columns with spiral packing have the least pressure drop. Of the operating conditions, the total throughput and the reflux ratio are the most important. With the same reflux ratio, the back-pressure can be used for measuring the throughput. As an example, the back-pressure in a column packed with 2.4-mm single-turn helices, 111 feet high and 0.79 inch in diameter, rate of boiling from 580 to 1,120 cc per hour at total reflux, is from 11 to 28 mm of mercury respectively.

Free Space and Hold-up

The free space of fractionating columns is the volume of the fractionating space not occupied by packing and usually expressed in per cent of the total volume. The free space predetermines the linear velocity of vapors; the greater the free space, the higher the efficiency of the column. A great free space and a large packing surface are necessary conditions for the efficiency of fractionating columns.

The hold-up of fractionating columns, or the total amount of vapor and liquid in the column under operating conditions, is another factor particularly important for the sharpness of separation of individual hydrocarbons or narrow fractions, which are present in small proportions. The quantity of each hydrocarbon or fraction distilled should be more than the hold-up of the column; otherwise, only a part of the column would be used for the fractionation of the hydrocarbons in question.

The hold-up of bubble-type columns is comparatively great, and may be as high as 300-500 cc in a column with 100 plates and a distillation rate 100 cc per hour. The hold-up of packed columns is in general small. For instance, Fenske *et al.*³² give the hold-up of a packed column (52 feet high and $\frac{3}{4}$ inch in diameter), producing 40 to 50 cc of distillate per hour at a 30:1 reflux ratio, as 50 cc only. Columns with spiral packing have a minimum hold-up. Fenske, Tongberg and Quiggle⁴⁰ give data (Table 18) on the free space and hold-up for various packings under comparable conditions.

Table 18. Free Space and Hold-up of Packed Columns.

Packing	Free Space, (%)	Hold-up (Ratio of Volume of liquid to volume of packing)
Miscellaneous carding teeth	92.1	0.023
G-turns N-24 Lucero wire helix	91.1	0.054
Single turn N-24 Lucero wire helix	82.0	0.046
$\frac{3}{32}$ " Carding teeth	81.6	0.042
N-16 single-link iron jack chain	72.3	0.033
Glass Raschig rings, 5 mm	69.8	0.037

Distillation Rate

The distillation rate, or production rate, equals to the quantity of product or distillate withdrawn from the column per minute or hour. This rate should not be confused with the evaporation rate, which is the amount of vapor evaporated in the still per minute or hour. The evaporation rate is greater than the distillation rate, the amount of difference depending upon the reflux ratio.

The distillation rate is predetermined by the square section of the column and the reflux ratio, assuming that the linear velocity of vapors remains approximately constant, and ensures equilibrium conditions in the bubble-cap plates or in the packed sections. The distillation rate of very efficient columns (100 theoretical plates, 10 to 20 mm in diameter, with a reflux ratio of about 100:1) is approximately 2 to 8 cc of distillate per hour. Thus, the operation is slow and time-consuming. Many days of

continuous operation are required for resolution of a sample into individual hydrocarbons or very narrow fractions.

Procedure of Fractionation

The separation of naphtha fractions of a Mid-Continent crude oil (Ponca City Field) for isolation of cyclohexane may be taken as a typical example of the application of the fractionation method (Bruun and Hicks-Bruun¹⁸). The crude oil is first distilled in a semi-commercial batch still provided with a column having 20 bubble-cap plates. The charge to the still is 200 gallons. Three charges of 200 gallons each are distilled to produce 4-gallon cuts. The cuts thus obtained are first redistilled twice in a still of 20 liters capacity, having a column with 20 bubble-cap plates. The lower-boiling fractions are then fractionated through a 30-plate "Pyrex" rectifying column, the distillation rate being about 2 cc per minute and the reflux ratio about 10:1. Finally, the fractions produced are redistilled with a 35-foot column packed with chromium-plated steel jack-chain. The rate of the last fractionation is about 1 cc per minute and the reflux ratio 10:1. As a result of these consecutive fractionations, the material is split into a number of 1°C cuts.

The application of the method to isolation of an individual hydrocarbon may be illustrated by the separation of cyclohexane from the same crude oil. Cyclohexane is concentrated in the cuts boiling from 74° to 85°C, which also contain benzene. Since the separation of benzene from cyclohexane by fractional distillation is practically impossible in view of the very close boiling temperatures (benzene 80.1°C and cyclohexane 80.8°C at atmospheric pressure), benzene was removed from the fractions by nitration. The remaining hydrocarbons were then subjected to five more fractionations. As a result, most of the material (about 7 liters) was concentrated in the cut boiling between 80° and 80.5°C. The properties of this cut compared with those of pure cyclohexane are:

	B. P. (°C)	Freezing Range (°C)	Refractive Index (N _D ²⁰)
Cut	80.4	-12 to -36	1.422
Cyclohexane	80.8	6.25(6.4)	1.4263

In view of the narrow boiling range of the cut, further separation of cyclohexane by fractional distillation would be impossible. Therefore, the final separation to the pure state was carried out by fractional crystallization.

Fenske and his co-workers^{82, 119, 123} showed that it is possible to separate straight-run gasolines in one fractionation into narrow fractions, some of which represent certain hydrocarbons of 85 to 90 per cent purity, by using columns corresponding to 70-75 theoretical plates (reflux ratio up to 40:1). For instance, a Michigan straight-run gasoline gave a normal pentane fraction with a boiling spread of 0.9°F, a normal hexane fraction with a boiling spread of 2.6°F, etc., as a result of such a fractionation.

A Yates (Texas) straight-run gasoline was separated in a 75-plate column (reflux ratio 35:1) into a series of narrow fractions, and the material boiling from 91.8° to 103.1°C was refractionated in a 100-plate column (reflux ratio 32:1). The second fractionation yielded 13.5 per cent of the charge of almost pure methyl cyclohexane. The total content of methyleyclohexane in the original Yates gasoline was 0.8 per cent. Thus the separation of this hydrocarbon in a practically pure state was possible as a result of two fractionations with very efficient columns.

A Michigan straight-run naphtha (b.r. 44° to 134°C) was fractionated in a column with 75 theoretical plates, reflux ratio 40:1, into 179 narrow fractions. The normal hexane fraction (12 per cent of the charge), with a boiling spread of 0.9°C, contained 90 to 93 mole per cent of pure normal hexane. The normal heptane fraction, comprising 12.4 per cent of the charge, contained about 85 mole per cent of normal heptane. Very pure normal nonane and normal decane fractions (more than 80 mole per cent of pure hydrocarbons) were also obtained by a single fractionation of a naphtha boiling at 157° to 200°C from the same crude.

Donald³⁰ and Watson and Spinks¹³⁹ used the following procedure for the fractional distillation of Canadian crudes. The first fractionation was carried out either in a Stedman packed column 3 inches in diameter and 2 feet long (charge 33.2 liters), or in a smaller column of the same type 1 inch in diameter and 3 feet long (charge 14 liters). The reflux ratio was from 10:1 to 20:1. Six or seven broad fractions were obtained as a result. These were refractionated (in some cases after treatment with sulfuric acid to remove aromatic hydrocarbons), either in the 5-foot column or in the 3-foot column described, the reflux ratio being much higher (up to 50:1 or more). The second fractionation in many cases produced hydrocarbons of purity better than 85 per cent.

Rossini *et al.*¹⁰⁶ described the results of fractionation of straight-run gasolines in two columns with Stedman and Heli-Grid packing, which were discussed above. The separation of a mixture of 17 known hydrocarbons in a similar column showed that the fractionation is practically quantitative, with negligible deviations from the percentage charged. Separation of the aromatics extracted from East Texas naphtha in such a column is illustrated in Fig. 7, which shows clearly the degree of separation. The isolation of benzene, toluene, ethyl benzene, para and meta xylenes, ortho-xylene, isopropyl benzene and n-propyl benzene is quite sharp. Above n-propyl benzene, the number of aromatic hydrocarbons is too great for a clear separation to be effected in one stage. Fractionation of paraffins and naphthenes separated from the aromatics by adsorption also gives very close results.

These investigations show clearly that the degree of separation of hydrocarbons by simple, efficient fractionation in modern columns is much greater than could be expected few years ago. It should be understood, however, that hydrocarbons which are present in the product to be fractionated in very small proportions (*e.g.*, less than 0.5 per cent),

cannot be obtained in a comparatively pure state after one or two fractionations, even with very efficient columns; they require the application of other methods of separation in conjunction with repeated distillations.

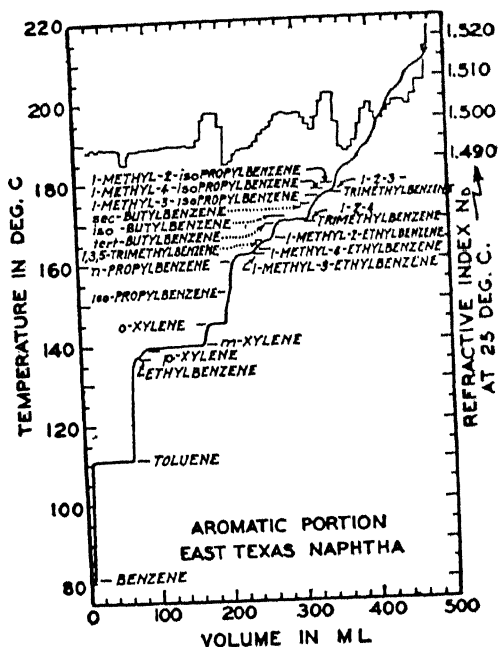


FIGURE 7. Plot of the boiling point and refractive index versus volume, for the distillation of the aromatic hydrocarbons from an East Texas naphtha. Distillation at 770 mm mercury. (Courtesy Petroleum Refiner)

High-vacuum Fractionation

Fractionation under atmospheric pressure is used for gasoline and kerosene distillates. The use of reduced pressures, however, is recommended in distillation of heavy naphthas and kerosenes. White and Glasgow¹⁸⁸ fractionated a naphtha of boiling range 130°-145°C at 215 mm of mercury, and Mair and Streiff⁷⁶ a kerosene distillate at 56 mm. The fractionation of high-boiling fractions is performed in a high vacuum.

Leslie and Heuer⁶⁸ studied the effect of change in pressure on the boiling points of lubricating fractions and found that a decrease in pressure from 40 to 10 mm decreases the boiling point on an average of 43°C; a further decrease from 10 to 1 mm decreases the boiling point about 40°C; but a decrease from 1 to 0.1 mm lowers it only 13°C. Thus, a pressure of about 1 mm should be considered the most practical in distillation, unless extremely low pressures in molecular stills or cathodic vacuum are used.

A small pressure drop is particularly important for vacuum distillation. Spiral packing, suspended jack-chain, or similar packing giving minimum pressure drop, is used in columns operating under very low pressure (1 mm of mercury, or less). The pressure drop in such columns about 1 meter high is less than 1 mm.

Mair, Schiektanz and Rose⁷⁵ described a vacuum fractionating column used by the Bureau of Standards for fractionation of lubricating-oil distillates. The glass column, 120 cm long and 2 cm in inside diameter, is provided with a spiral packing of No. 8 copper wire. The column was surrounded by a jacket, *i.e.*, a larger glass tube insulated with asbestos and equipped with electrical heating, to counterbalance the heat losses. It was sealed to a "Pyrex" flask which served as a still pot, heated electrically. The top of the column was connected with a bulb which was open to air and served as a condenser. The column was connected with a McLeod gage and a mercury-diffusion pump. The pressure of 10^{-4} mm of mercury or less at the head of the column could be maintained in distillation. Leslie and Heuer⁶⁸ described a continuous high-vacuum still operating under the same low pressure.

Fractionation under Varied Pressure

The separation of two (or more) hydrocarbons which have almost the same boiling points at atmospheric pressure can be effected by fractionation under varying pressures. The pressure may be higher or lower than atmospheric. Lower pressures are customarily used.

The effect of pressure on the boiling point varies for different hydrocarbons. The decrease in the boiling point of the aromatic hydrocarbons with decreasing pressure is more rapid than that of the naphthenes, and that of the naphthenes is more rapid than that of the paraffins. Thus, two hydrocarbons, for instance, a paraffin and an aromatic, boiling at the same temperature at atmospheric pressure, will have a spread in their boiling temperatures as the pressure is reduced. The greater the reduction in the pressure, the wider the spread.

In some cases the spread between the boiling temperatures of two hydrocarbons is greater at 1 atmosphere than at reduced pressures. In such cases elevated pressures may be used. In general, constant-boiling mixtures may be separated into individual hydrocarbons by fractionation at a pressure different from that causing the constant-boiling behavior. According to Rossini, Mair and Glasgow,¹⁰⁴ the spread in the boiling points for a paraffin and an aromatic of the same boiling point at 1 atmosphere is about 5°C when the pressure is reduced to 0.075 atm. Under the same conditions the spread for a naphthenic and an aromatic hydrocarbon of the same boiling point is only 2°C.

Thus separation of two hydrocarbons, an aromatic and a paraffin or a naphthene and a paraffin, boiling at the same temperature at 1 atm., may be quite feasible at 0.075 atm. in a column with 100 or more theoretical plates.

Azeotropic Distillation

Azeotropic distillation is also widely used for separating mixtures of two (or more) hydrocarbons or other components of approximately the same boiling points. Azeotropic mixtures of two components can also be separated by this method. A third component, which forms constant-boiling azeotropic mixtures with two hydrocarbons to be separated, is added. Distillation of the new mixture with the third component gives a first distillate, consisting of an azeotropic mixture of one hydrocarbon with the added component, and then a second distillate consisting of an azeotropic mixture of the second hydrocarbon with the same component. The azeotropic mixtures formed by the first and by the second hydrocarbon must have an appreciable spread in boiling temperatures if a satisfactory separation is to be achieved.

A classic example of such a separation is the production of anhydrous ethyl alcohol from the azeotropic (constant-boiling) mixture of alcohol and water (95.6 and 4.4 per cent by weight, respectively), which boils at a constant temperature (78.1°C) and thus cannot be separated by fractionation. This azeotropic mixture is broken up by the addition of benzene, which forms a ternary azeotropic mixture with ethyl alcohol and water and a binary azeotropic mixture with ethyl alcohol. These ternary and binary azeotropic mixtures are first distilled; this is followed by distillation of absolute ethyl alcohol.

As has been started above, the constant-boiling mixtures of two or more hydrocarbons are usually not azeotropic mixtures, as in the case of ethyl alcohol and water, but simple mixtures of the closely boiling individual hydrocarbons forming the mixture, the separation of which by fractional distillation is impossible, even with highly efficient fractionating columns corresponding to 100 or more theoretical plates. It should be remembered that about 125 theoretical plates are required for separation of two hydrocarbons differing by 2°C in their boiling points close to 100°C . Thus hydrocarbons having a difference in boiling point of less than 1°C cannot be separated by fractional distillation even in the most efficient laboratory columns.

It has been accepted by many authors that paraffins and naphthenes form true azeotropic mixtures with aromatic hydrocarbons, for instance, normal hexane and benzene. Tongberg and Johnson¹²¹ found, however, that these hydrocarbons do not form an azeotropic mixture, but exhibit an unusual distillation relationship. At concentrations below 3.5 mole per cent both the vapor and liquid phases of benzene have about the same composition, so that separation by fractionation is impossible. Tongberg, Fenske and Sweeney¹²⁰ also failed to find true azeotropic mixtures of hydrocarbons.

The deviations of such systems as benzene-cyclohexane from ideal mixtures are not at all clear. But the formation of azeotropic mixtures by certain hydrocarbons cannot be ruled out, in view of the difficulties

encountered in detecting azeotropic mixtures boiling close to the boiling point of one of the components. Griswold and Ludwig⁴⁶ found that methyleyclopentane and benzene have a slight tendency to form an azeotropic mixture corresponding to 90 per cent methyleyclopentane and boiling at 71.5°C (boiling point of methyleyclopentane is 71.8°C). These authors suggest that the abnormal behavior of the system benzene-cyclohexane may be due also to the formation of an azeotropic mixture with a boiling point within 0.1°C of that of pure cyclohexane.

The abnormal behavior of aromatic-naphthene and aromatic-paraffin systems on distillation is a serious drawback to the separation of hydrocarbons by fractional distillation. Rossini *et al.*¹⁰⁶ found that preliminary separation of aromatics by adsorption or other conventional methods enormously facilitates the quantitative separation of naphthenes and paraffins by fractional distillation. Fractional distillation of the aromatic portion is also simplified.

Griswold, Van Berg and Kasch⁴⁷ not only confirmed the beneficial effect of the removal of aromatics for the separation of hydrocarbons but suggested preliminary separation of paraffin-naphthene mixtures into (predominantly) paraffinic and (predominantly) naphthenic portions by solvent extraction. Fractional distillation of the two portions produces a more effective separation of hydrocarbons than that of the whole mixture. This is particularly important for the separation or detection of hydrocarbons present in small proportions. For example, by this method 3-methylpentane was found to be practically absent from the hexane fraction of a natural gasoline, whereas fractionation of the whole sample without preliminary solvent extraction of naphthenes produced narrow cuts having the properties of 3-methylpentane.

Practically all polar organic compounds form azeotropic constant-boiling mixtures with all hydrocarbons of a lower boiling point than that of the original hydrocarbon. The spread between the original boiling point and the boiling point of the azeotropic mixture is greatest for paraffins and least for aromatics, naphthenes being intermediate. Thus the separation of a constant-boiling mixture of a paraffin and an aromatic by azeotropic distillation is easier than that of a paraffin and a naphthene. The composition of the azeotropic mixture usually varies from 20 to 60 mole per cent of hydrocarbon.

According to Mair *et al.*⁷² and Rossini,¹⁰⁴ azeotropic distillation in rectifying columns of from 50 to 100 theoretical plates can separate by one or more distillations mixtures of narrow-boiling aromatics with naphthenes or paraffins; those of naphthenes with paraffins; those of aromatics of different degrees of "aromaticity," and those of naphthenes of different degrees of "naphthenicity." By the degree of "aromaticity" or "naphthenicity" is meant the proportion of aromatic or naphthenic rings versus paraffinic side chains (and naphthenic rings in an aromatic hydrocarbon).

Kayes⁵⁸ pointed out that the formation of constant-boiling azeotropic mixtures is not a prerequisite for the use of the third component in frac-

tionation. Generally speaking, the third component reduces the partial pressure of one of the components to be separated to a greater extent than it does that of the other.

In the following table are the boiling points of benzene and cyclohexane, as well as those of the azeotropic mixtures of these hydrocarbons with methyl alcohol:

	B. P. of Hydrocarbon (°C)	B. P. of Azeotr. Mixture (°C)	Mol. Per Cent of Hydrocarbon
Benzene	80.1	58.34	61.4
Cyclohexane	80.8	54.2	61.0

Thus the spread between the boiling points of benzene and cyclohexane (0.7°C) considerably increases (4.1°C) for the azeotropic mixtures of these hydrocarbons with methyl alcohol. The order of volatility of the azeotropic mixtures is reversed as compared with the original hydrocarbons.

The azeotrope-forming substance used for azeotropic distillation must have a boiling point near that of the hydrocarbon mixture. The difference in the boiling points should not exceed 50°C. The azeotrope-forming substance should be completely soluble in the hydrocarbon mixture at the boiling and condensation temperatures; or, in other words, the solubility should be complete in all distillation and fractionating parts of the fractionating equipment.

The azeotropic mixtures of hydrocarbons and polar azeotrope-forming substances can be broken up most easily by dilution with water, which dissolves the polar substance used. With an excess of water the solubility of the hydrocarbons in the polar substance-water layer, as well as the solubility of the polar substance in the hydrocarbon layer, is negligible, so that the separation of the hydrocarbons is practically complete. Thus the azeotrope-forming substance must be completely miscible with water.

Treatment with water is preferred because of the availability of water. It is understood, however, that any appropriate solvent or reagent immiscible with hydrocarbons and miscible with a polar azeotrope-forming substance can be employed instead of water. Brane and Hunter,¹⁵ for example, used aniline as an azeotrope-forming component which was removed by treatment with aqueous hydrochloric acid.

Procedure for Azeotropic Distillation

Brane and Hunter¹⁵ investigated the azeotropic distillation of hexane and cyclohexane in the presence of methyl alcohol, amyl alcohol, aniline and aniline plus methyl alcohol. The best results were obtained with aniline. An equal volume of aniline is added to the mixture. Plain fractionation of a 50/50 mixture of cyclohexane and benzene into five fractions gives very incomplete separation: the content of cyclohexane in the fractions varies from 33.3 to 64 per cent. With the addition of aniline, fractionation in the same apparatus gave much better separation, and the content of cyclohexane in the corresponding five fractions varied from

19 to 98 per cent. The authors used azeotropic fractionation with aniline for separation some individual paraffins and naphthenes in a cracked gasoline. Tonberg and Johnston¹²¹ recommended tertiary butyl alcohol as an azeotrope-forming substance for the separation of such mixtures as benzene-normal hexane.

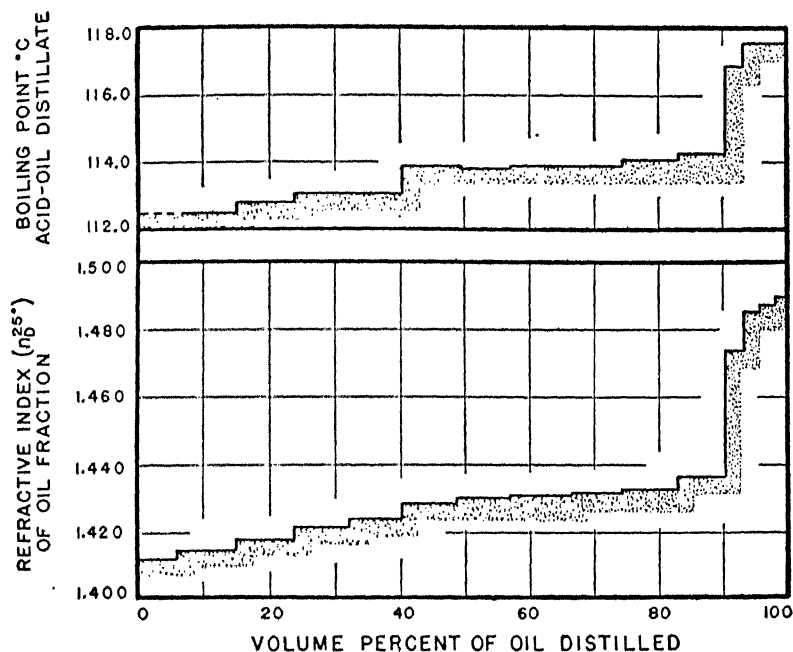


FIGURE 8. Azeotropic fractionation of a petroleum fraction boiling between 110.5 and 111.0°C at 215 mm mercury with acetic acid. (Courtesy *Journal of Research of the National Bureau of Standards*)

Schickentanz¹¹⁰ described the azeotropic distillation of a narrow fraction boiling between 122° and 123°C at 215 mm pressure. Plain fractionation into 28 subfractions does not give satisfactory results. The refractive index of these subfractions varies erratically between 1.4212 and 1.4259. The fraction is then combined with three volumes of glacial acetic acid and separated into 19 subfractions. An excess of the azeotrope-forming substance is required in order to have pure acetic acid remaining in the still pot after all the hydrocarbons are distilled off. The acid is removed from each subfraction by washing with water. The subfractions show a gradual increase in refractive index from 1.4132 to 1.4409. Thus, according to the general rule, paraffinic hydrocarbons have lower boiling points in their azeotropic mixtures and distill at lower temperatures in the first subfractions. The last subfractions are enriched with naphthenes. A complete separation of hydrocarbons was not obtained, probably because of the formation of ternary azeotropic mixtures.

Another example of the use of acetic acid as an azeotropic-forming component was given by Rose and White.¹⁰¹ A fraction boiling between 110.5° and 111.0°C at 215 mm pressure (154° at 760 mm) was fractionated with acetic acid (3½ volumes per volume of the fraction). The results are given in Fig. 8. The upper graph represents the boiling points

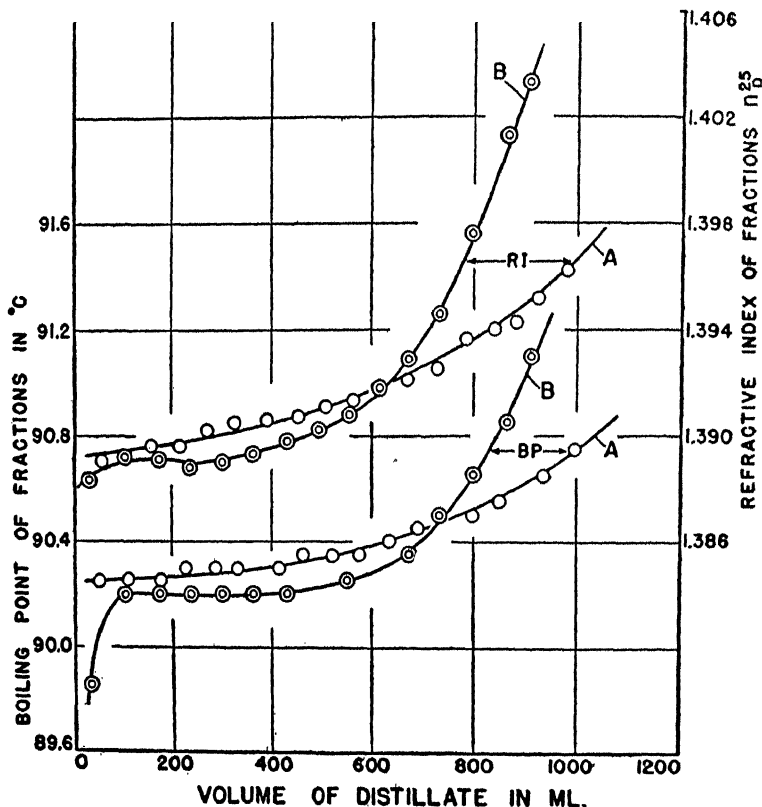


FIGURE 9. Normal and azeotropic fractionation of a petroleum fraction. Fractionation of the paraffin-naphthene mixture by distillation at normal pressure is contrasted to the fractionation of the oil by azeotropic distillation with methyl alcohol. The curves marked A refer to the oil fractions from normal distillation and the curves marked B refer to the oil fractions obtained from azeotropic distillation. The scale of ordinates in the figure gives on the left the boiling points and on the right the refractive indices for the oil fractions from the two distillations.

of subfractions in the azeotropic distillation. The data show that the spread between the aromatic and paraffinic parts of the 0.5°C fraction reaches 5°C. The lower graph gives the refractive index of the subfractions freed from acetic acid. Both graphs, particularly the lower one, show clearly the gradual separation of naphthenes from paraffins in the subfractions up to 90 per cent overhead and a very sharp separation of aromatics.

Glasgow⁴⁴ described the azeotropic distillation of a paraffin-naphthene fraction boiling between 90 and 91.2°C, consisting mostly of 2-methylhexane and *trans*-1, 3-dimethylcyclopentane. Methyl alcohol was used as an azeotrope-forming component. The volume ratio of methyl alcohol to the fraction was 2:1. The results of normal fractionation (A) and of azeotropic fractionation (B) are given in Fig. 9. The curves show clearly a much sharper separation in the case of azeotropic distillation.

The following azeotrope-forming substances have been successfully used in the laboratory of the National Bureau of Standards (Rossini, *et al.*¹⁰⁴):

	Boiling Point at 1 Atm (°C)
Methyl alcohol	66
Ethyl alcohol	78
Methyl cyanide	82
Acetic acid	118
Ethylene glycol monomethyl ether acetate	143
Ethylene glycol monobutyl ether	171
Diethylene glycol monomethyl ether	193

Polar substances are added as azeotrope-forming components to mixtures of narrow-boiling hydrocarbons. On the contrary, hydrocarbons can be added to mixtures of narrow-boiling polar components to effect separation of the latter by azeotropic fractionation. Bratton, Felsing and Bailey¹⁴ found that the fractionation of nitrogen bases extracted from petroleum is enhanced by inert hydrocarbons, which are added to the nitrogen bases in the quantity of 15 to 20 volumes ("amplified distillation"). The nitrogen bases in such mixtures are distilled considerably below their boiling points because of the formation of minimum-boiling azeotropic mixtures. The spread in the boiling points of the azeotropic mixtures may be considerably greater than in the case of the pure nitrogen bases.

Distillation in Molecular Stills

The common feature of distillation at atmospheric pressure or under high vacuum is the formation of vapor by boiling. As a result, the temperature even in high-vacuum distillation may be comparatively high for high molecular-weight hydrocarbons, or other compounds of crude oils. For example, the distillation temperature of heavy residues at 1 mm pressure may be as high as 300°C or even more. Many hydrocarbons, particularly some oxygen-containing compounds, partially decompose under such temperature conditions.

Distillation in molecular stills differs substantially from the above methods by complete elimination of the boiling process. The distillation takes place by evaporation of the product to be distilled from a large heated surface under high vacuum and by condensation of the vapor on another large surface cooled to a proper temperature. The vacuum is about 0.001 mm or lower. The distance between the heated and cooled surfaces corresponds to the mean free path of molecules under the vacuum

conditions. For instance, the free path of atmospheric molecules is 5.65 cm at 0.001 mm pressure. Accordingly, the distance between the surfaces under such a pressure should be of this above order.

The temperature of the "heated" surface ranges from room temperature to 100°C or more. The distillation rate depends upon the difference in the vapor pressure of the substance to be distilled at the temperatures of the heated and cooled surfaces. Thus the cooling must be very efficient and may be effected by Dry Ice or liquid air, if the heating temperature is low. In continuous operation the product to be distilled is passed to the heated surface, where it forms a thin film which gives off the vapor.

Houghton⁵⁶ found that distillation under the conditions described can be used for a certain degree of separation of paraffinic and naphthenic or aromatic constituents of high-boiling fractions. He recommended distilling or vaporizing molecules from a film of liquid oil at very low pressures, less than 100 microns, and condensing the vapors in close proximity to the vaporizing surface, so that the distance between the vaporizing and condensing surfaces should be of the order of the mean free path of the vaporized molecules. Narrow fractions boiling in the range of 300°F, or preferably less at 10 mm pressure, can be separated by the method in question into more "paraffinic" and more "naphthenic" fractions. Fig. 10 represents an apparatus for continuous short-path distillation. The oil of a narrow boiling range enters through valve (1) into an electrically heated degassing unit (2) wherein the oil is heated to a temperature of 175° to 300°F under a pressure of about 2-15 mm. The degassing unit (4) is maintained at the same temperature but at a reduced pressure of 50 to 150 microns. The oil then enters unit 6 operating at the same reduced pressure and at the same or slightly higher temperature. The heated oil is introduced upon the upper end of a tubular member (11) of the still. This member is heated internally by resistance heater (12) and is provided externally with a spiral (13) to effect uniform distribution of the oil over the surface. The tubular member (11) is surrounded with a jacket (14) provided with a series of gutters (15) which are the outlets for the distillates condensed on the surface of the jacket. The gutters are connected with receivers (17) and vacuum pumps. The jacket (14) is surrounded by a second jacket (20) through which a cooling medium is circulated. The distance between the jacket (14) and the tubular vaporizing member (11) is of the order of 2 inches or less. The low pressure of about 50 microns or less is maintained within the jacket (14) and receivers (17). A line (21) and a freeze-out trap (22) (carbon dioxide and acetone) are provided to condense any volatile materials passing from the top of the still.

The vaporization of oil takes place progressively from the upper end of the tubular member (11) to the lower end. The unvaporized residuum is withdrawn through lines (16) and receivers (17).

Under the above very low pressures, the partial pressure of the aromatic and naphthenic components is considerably greater than that of

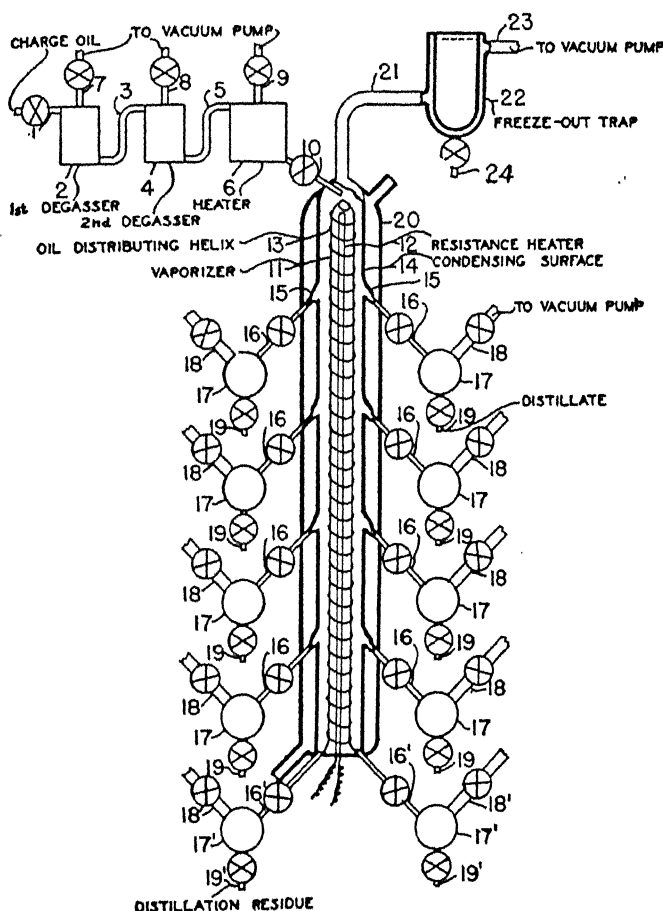


FIGURE 10. Molecular still.

the paraffinic components. Thus the first (upper) fractions are more naphthenic, whereas the last fractions and the residuum are more paraffinic. The data of Table 19 illustrate the separation effect.

Table 10. Fractionation in Molecular Still.

Stock: vacuum distillate from East Texas residuum, boiling range 500° to 700°F at 10 mm pressure.

Distillation conditions: pressure 4.1 microns, maximum distillation temperature 392°F

	Charge	-Fractions-					Bottoms
		2	3	4	5		
Yield (% by vol.)	100.0	18.3	17.8	12.5	8.9	8.0	34.5
A.P.I. gravity	20.6	18.3	19.9	21.0	21.7	21.7	21.6
S.U.V. at 130°F	689	403	550	571	590	650	1,233
S.U.V. at 210°F	100	70	83	89	93	100	159
Viscosity-gravity constant	0.861	0.885	0.866	0.860	0.854	0.853	0.844
Viscosity index	31	-14	4	25	43	47	71
O.D. Color	661	170	195	248	314	327	1,799

The separation of hydrocarbons of the same boiling point or vapor pressure by molecular distillation is possible because the rate of evaporation is inversely proportional to the square root of the molecular weight. Aromatic hydrocarbons have a lower molecular weight than naphthenes and paraffins of the same boiling point, and therefore are separated in the first fractions.

Riegel, *et al.*,⁹³ Quackenbush and Steenbock,⁹⁰ and Wollner *et al.*^{140d} have recently described the technique of laboratory molecular distillation. It should be pointed out that the technique of the molecular distillation has been enormously improved during the last few years in connection with distillation of high molecular weight compounds, particularly vitamins. In such distillations the pressure is from 1μ to 0.001μ . The method of the falling film, described above, has been replaced by the use of centrifugal force. The liquid product is introduced to the center of the disc rotating at 4,000-5,000 rpm and is thrown off to the periphery of the disc. As a result, the product is spread on the surface of the disc as a thin film, is then evaporated and condensed on a cold plate facing the rotating disc. The disc may be heated to any desired temperature. To the best knowledge of the author, this method has not been applied to the distillation of high molecular weight constituents of petroleum.

Crystallization

Crystallization, one of the most efficient methods of separating and identifying organic compounds, is being used in petroleum chemistry to only moderate extent. There are two drawbacks to the wide application of this method. First, the hydrocarbons of low and moderately boiling fractions usually have very low melting points; operations at such low temperatures require special and elaborate methods. Secondly, many oil hydrocarbons form glassy or gelatinous systems at low temperatures precluding crystallization or separation.

There are a few hydrocarbons in petroleum products and fractions which have a comparatively high melting point (above 30°C). To these belong: high molecular weight paraffins (particularly of normal structure), naphthalene, certain methyl derivatives of naphthalene, and certain derivatives of anthracene and phenanthrene. The melting point of benzene and cyclohexane is 6°C . Other oil hydrocarbons, even of high molecular weight, have melting points much below -10°C .

The separation by crystallization of such hydrocarbons as naphthalene or solid paraffins has been used extensively and has not involved any particular problems. Such hydrocarbons are separated by crystallization, either directly from appropriate fractions or frequently after diluting the fraction with a solvent. Dilution by a solvent is necessary for comparatively high-boiling fractions, which become very viscous at low temperatures and preclude both crystallization and separation. For instance, naphthalene is easily crystallized on cooling from the appropriate fraction boiling in the range of 215° to 225°C . This fraction is not

viscous, even at low temperatures, and no dilution with any solvent is required for crystallization. The separated raw naphthalene can be purified by recrystallization, for example, from benzene or alcohol.

Crystallization and Separation of Petroleum Wax

Solid paraffins or petroleum waxes are crystallized in comparatively viscous distillates. The viscosity of these distillates at low temperatures may be enormous. In addition to this, the crystalline paraffins form with oils congealed systems, the separation of which presents great difficulties. The paraffins separated from the oil contain a large percentage of oil, which may be as high as 50 per cent with respect to the total filtered product. Accordingly, the crystallization of solid paraffins or petroleum waxes takes place in the presence of certain non-viscous solvents which facilitate crystallization and separation of the hydrocarbons. Any free-flowing substance miscible with liquid petroleum hydrocarbons can be used as a solvent, as, for instance, liquid propane, butane, petroleum ether, ethyl ether, chlorinated hydrocarbons, etc.; but the solvent must have a very low melting point to make operation at low temperatures possible.

To overcome the difficulties caused by the high viscosity of oils at low temperatures, it is necessary to use a comparatively large excess of solvent with respect to oil—of the order 5 to 1. As a result, the solubility of solid paraffins correspondingly increases, affecting the degree of separation. Thus the crystallization and separation of solid paraffins from the mixture of the solvent and oil is carried out either at very low temperatures or in the presence of another substance miscible with the solvent but precipitating solid paraffins *e.g.*, ethyl alcohol, acetone, etc. It should be noted, however, that the compounds mentioned may precipitate not only solid paraffins but also the oil mixed with the solvent, since the solubility of heavy oils in low molecular weight alcohols and ketones is limited at low temperatures. Thus the proportion of a precipitating substance to a solvent should ensure the precipitation of solid paraffins and should not cause separation of the oil. Some compounds, such as butanone, can be used individually instead of mixtures, since they contain a comparatively long paraffinic side chain and a ketone group, and thus combine the properties of a solvent for oils and a precipitating agent for solid paraffins.

Some of the numerous methods of determination and separation of solid paraffins (petroleum wax) are described below.

Engler-Holde Method.⁵⁵

From 3 to 10 grams of distillate are completely dissolved in 50 cc of ether-alcohol mixture (1:1). The total quantity of precipitated petroleum wax should be from 50 to 100 mg. The solution is cooled to -20°C , and the paraffins crystallized are filtered at the same temperature under suction and washed with 5 cc of ether-alcohol. The precipitate is dis-

solved in warm petroleum naphtha (boiling range from 60 to 80°C) and the filter is washed thoroughly with the same naphtha. The naphtha is then evaporated, and the wax dissolved in 15 cc of water-free acetone on boiling and then cooled to +15°C. The solid paraffins are filtered and washed with 10-15 cc of acetone at the same temperature. The paraffins then are dissolved in the same naphtha and transferred to a beaker (50 cc), in which the naphtha is evaporated. The solid paraffins are dried at 105°C for 15 minutes and weighed.

Schwarz-von Huber Method.⁵⁵

From 1 to 5 grams of distillate are dissolved at room temperature in the smallest possible amount of butanone (sp. gr. 0.812 at 20°C) containing 1.3 per cent of water. The solution is cooled to -20°C. More butanone is added to keep the oils in solution; only the flakes of paraffin wax should be visible. Separation by filtration is carried out at from -15 to -20°C. The residuum is repeatedly washed with 5-10 cc of cold butanone (sp. gr. 0.812) at the same temperature until several cc of the washing liquid leave no trace of oil after evaporation. Usually 4 or 5 washing operations are sufficient. The solid paraffin then is dissolved in hot naphtha and treated as in the previous method.

Knowles and Levin⁵⁹ recommended the use of methyl isobutyl ketone or hexone as a solvent for crystallization and precipitation of petroleum wax. Like butanone, this solvent possesses high solvent power for oils.

These methods can be applied only to distillates. Residual products containing a large proportion of resinous and asphaltic materials, when treated with alcohols or ketones, precipitate resins and asphaltenes, as well as very heavy oils which are mixed with precipitating paraffins. The resins and asphaltenes must be removed before the separation and precipitation of solid paraffins. Sulfuric acid may be used for this purpose. The residual product is diluted with a light gasoline, volume for volume. The blend is treated with an equal volume of 98-100 per cent sulfuric acid in a funnel and shaken for 30 minutes. The mixture is left for 24 hours. After separation of the sludge, the refined residuum and gasoline are washed with water and dried. The gasoline is removed by distillation. The residuum, freed from resinous and asphaltic materials and heavy aromatic oils, is analyzed in the same manner as the distillates.

Betts and Wirsig¹⁰ recommend aluminum chloride (10 gr. per 20 gr. asphalt dissolved in 200 cc naphtha) for destroying resins and asphalts. The results are either close to those obtained with sulfuric acid or substantially lower because of the sulfonation effect of sulfuric acid and contamination of petroleum wax with the sulfonates formed, according to the authors. McKittrick, Henriques and Wolff⁸¹ crystallize petroleum wax from ethylene dichloride at -35° or from chloroform at -55°. Ethylene dichloride is preferred, but it cannot be used for highly paraffinic oils which are not sufficiently soluble in this solvent at low temperatures. For such oils chloroform is suitable. Samples of one to two grams

of oily wax are dissolved in 75 cc of solvent, and the crystallization and separation take place at the temperatures given above. However, crystallization can be performed in many stages to facilitate the filtration, and in such a case the final crystallization and filtration are carried out at the minimum temperature. This method usually gives higher figures than the above methods due to the separation of low-melting point waxes. By its use, waxes melting from 30 to 20°C can be separated. The low temperatures used in this method are due to the absence of any other solvent which would decrease the solubility of petroleum wax. The method described can be applied directly to crudes and residues unless the content of asphaltic and resinous materials is too great. It should be kept in mind that the solubility of resins and asphaltenes in chlorinated solvents is comparatively great even at low temperatures. However, the absorption of these materials by petroleum waxes at very low temperatures is not to be neglected.

Such solvents as liquid propane and butane, can be used for crystallization and separation of petroleum wax at low temperatures, but the precipitating power of these solvents with reference to asphaltic and resinous components and heavy oils should be taken into consideration (Chapter 9). As a result, the petroleum wax crystallized from such solvents will be contaminated with the above components, particularly when the wax is separated from heavy residues.

It is obvious that preliminary dry distillation of crudes or residues before separation of solid paraffins cannot be employed, since this distillation is accompanied by cracking. As a result, a considerable part of the original high-molecular weight paraffins is cracked or converted to paraffins of a lower molecular weight. This method is, however, frequently used for the approximate determination of petroleum wax in crudes and residues. The proportion of high molecular-weight solid paraffins which is cracked in the dry distillation is usually 30 per cent, and may be as high as 50 per cent.

It should be clearly understood that the separation of solid paraffins described above is not necessarily their quantitative determination. As a matter of fact, the quantitative determination of solid paraffins *per se* is a somewhat indefinite problem. There is no strict border-line between solid and liquid paraffins or, in general, hydrocarbons. As a result, the quantitative effect of the separation of solid paraffins depends largely upon the temperature as well as upon the solvent used.

When the same solvent is employed, the temperature of crystallization (and filtration) predetermines the yield of solid paraffins. The lower the temperature, the higher the yield and the lower the average molecular weight and melting point of the paraffins.

According to Engel, the Separator-Nobel Company³³ uses the following method for determining the yields of petroleum wax or dewaxed oil versus the temperature. The oil (asphalt-free) to be tested in the amount of 75 cc is diluted with 225 cc of normal gasoline (boiling range from 60

to 95°C, A.P.I. from 58 to 62°), cooled to -20°C and filtered. The filter-residuum is washed at least three times with 75 cc of normal gasoline at the same temperature until three drops of the wash filtrate leave no oily residue after evaporation of gasoline. The filtrate and filter-residuum are separated from the gasoline by evaporation, and then the melting point of wax and the pour point of oil are determined. The same operation is repeated at -10, -30 and -40°C. The yield of petroleum wax depends upon the melting point of the wax; likewise the yield of dewaxed oil depends upon the pour point of the oil, as Fig. 11 clearly shows.

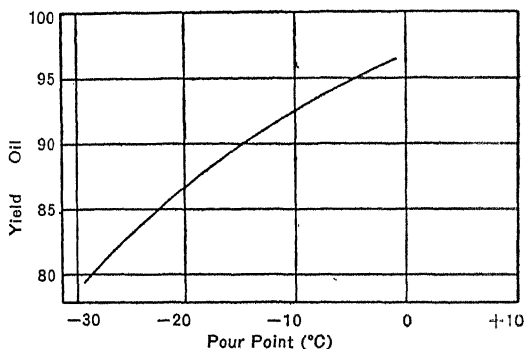


FIGURE 11. Yield of dewaxed oil versus pour point.

The yield of petroleum wax also varies with the nature of the solvent. Table 20 contains the data for the petroleum wax content of the same Mid-Continent bright stock, Duosol-treated, determined with varied solvents.

Table 20. Content of Petroleum Wax (Solid Paraffins) in a Mid-Continent. Bright Stock, Determined by Various Methods.

Method	Solvent	Temperature of Separation	Petroleum Wax (%)
A.B. Separator-Nobel	Normal gasoline	-40°C	13.0
" " "	"	-22°	5.7
Engler-Holde	Ether-alcohol	-20°	7.5
Schwarz-von Huber	Butanone	-15°	21.4
McKittrick <i>et al</i>	Chloroform	-55°	18.3

The solid paraffins separated by the methods described may be fractionated by distillation or by fractional crystallization from an appropriate solvent or by both operations. The latter process does not differ from the conventional operation.

It is of interest to note that the modern commercial methods of manufacturing paraffin wax are closer to the laboratory methods described than they were few years ago. The old method involved the filtration of chilled paraffin distillate, which produced slack wax containing up to 30 per cent of oil. The slack wax was freed from the oil in the process of sweating, which gave comparatively small yields of deoiled scale wax. Modern methods use either liquid propane or an appropriate mixture of

benzene and acetone (methyl ethyl ketone) as a solvent. As a result, slack wax having a small content of oil can be obtained. The sweating process may be entirely avoided or reduced considerably by a second recrystallization from the same solvent.

Crystallization and Separation of Low Molecular Weight Paraffins and Other Hydrocarbons

The crystallization and fractionation by crystallization of low molecular weight paraffins, as well as other hydrocarbons, has been used successfully by the National Bureau of Standards. It is well known that the melting points of normal paraffins are much higher than those of isoparaffins or mono-substituted naphthenes of the same molecular weight or boiling point. Table 21 gives some data on the melting points of normal paraffins and mono-substituted naphthenes boiling around 70, 100 and 130°C.

Table 21. Melting Points of Normal Paraffins and Naphthenes.

Hydrocarbon	Boiling Point (°C) at 760 mm	Melting Point (°C)
<i>n</i> -Hexane	68.8	-94.0
Methylcyclopentane	71.9	-142.2
.....
<i>n</i> -Heptane	98.4	-90.5
Ethylcyclopentane	103.4	-137.9
Methylcyclohexane	100.3	-126.3
.....
<i>n</i> -Octane	125.6	-56.8
Propylcyclopentane	130.8	-121
Ethylcyclohexane	131.8	-120

Since the difference in the melting points of these hydrocarbons is more conspicuous than in the boiling points, separation of the mixtures by fractional crystallization may be quite feasible. The melting points of isoparaffins also differ considerably from those of normal paraffins of the same boiling range (compare Chapter 6). Thus the method of fractional crystallization can successfully be applied to the separation of normal paraffins from other hydrocarbons in many narrow fractions.

It must be understood that any mixture of hydrocarbons having substantially different melting points can be separated by the method in question. In addition to normal paraffins, such hydrocarbons as cyclohexane, some other cyclohexane derivatives and aromatic hydrocarbons, have been fractionated by crystallization from appropriate fractions.

Crystallization of low molecular weight hydrocarbons at very low temperatures frequently has the same drawback as the crystallization of petroleum wax. Due to the high viscosity of hydrocarbons at very low temperatures, crystallization may be inhibited or may produce glassy systems which cannot be separated by filtration. As in the case of petroleum waxes, crystallization and separation can be encouraged by the addition of substances which decrease the viscosity at low temperatures. As diluents or solvents, such hydrocarbons as liquid methane, ethane,

propane, or their mixtures, as well as some halogenated hydrocarbons, can be used successfully.

The apparatus for fractional crystallization of low molecular weight paraffins and other low melting point hydrocarbons at very low temperatures consists of a metal cylinder provided with a stirrer (Leslie *et al.*⁶⁶). The metal cylinder is cooled by means of a slush of solid carbon dioxide with chloroform, etc. Liquid air also can be used. A Dewar tube or a special insulated bath is employed for the cooling medium. The cylinder is adapted also for filtration. For this purpose the bottom of the cylinder is provided with a copper gauze filter (200-mesh) covered by a heavy brass disk with a leather seal. The brass disk has a brass rod for withdrawing the disk. When crystallization is begun, the disk is on the filter; after it is finished, the disk is withdrawn from the filter, and the filtration takes place under suction or pressure. Thus crystallization and filtration are carried out in the same apparatus.

Another apparatus has been described by Leslie.⁶⁷ In this, crystallization and filtration are separate. The former is carried out in a metal cylinder with a stirrer, cooled as described above. Filtration takes place in a special centrifuge cooled to the desired temperature. The material crystallized in the crystallizer is thrown rapidly into the rotating drum of the centrifuge, the cylindrical walls of which are made of perforated brass and lined with fine linen cloth. As a result of the rapid motion of the rotating drum, the "mother liquid" passes the filter and thus is separated from the crystals. The mother liquid represents the first fraction separated. The dry crystals are scraped from the inside wall of the drum into the cone-shaped bottom of the centrifuge and allowed to melt to a desired extent. The drum is rotated again, and a second "mother liquid" or fraction is separated, and so on.

A few examples of crystallization without solvents and with solvents are given at this point. The *n*-octane fraction of refractive index 1.408 was fractionated by crystallization by Leslie and Schickltanz.⁶⁸ Fig. 12 represents the refractive indices of the cuts produced. It shows clearly the enrichment of the cuts with *n*-octane (refractive index 1.3975). The fraction of refractive index 1.397 contained 98 mole per cent of normal octane.

The procedure for fractional crystallization of the narrow cyclohexane fraction, boiling between 80.0 and 80.5°C and freezing between -12 and -30°C, has been described by Bruun and Hicks-Bruun.¹⁸ This fraction (7,200 cc), freed of benzene, was further separated by a great number of meltings into four fractions indicated by the large circles (Fig. 12). The temperature in each circle gives the initial freezing point. By further crystallization each of the three fractions freezing from -12 to -2.5°C was split up into three or four fractions. Those having nearly the same freezing points were combined and subjected to further fractional crystallization. The final results can be seen from Fig. 13 and Table 22. The figures of Table 22 illustrate the degree of purity of individual hydrocar-

bons obtainable by repeated fractional crystallization under appropriate conditions.

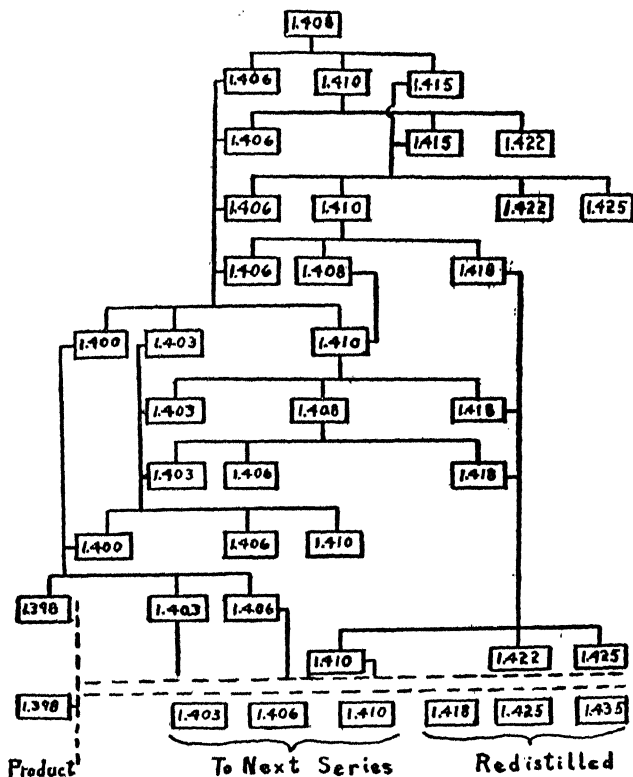


FIGURE 12. Fractional crystallization of normal octane. (Courtesy *Journal of Research of the National Bureau of Standards*)

Table 22. Cyclohexane Isolated from Petroleum by Fractional Crystallization.

Fraction (cc)	Initial Freezing Point (°C)	Purity (Mol per cent)
(Pure cyclohexane)	6.5	100
200	6.25	99.96
200	6.2	99.94
200	6.1	99.91
500	6.0	99.88
600	5.7	99.77
700	3.0	98.88
1,400	1.0	98.22
1,100	-7	95.58

Other fractions cannot be crystallized without a solvent. For instance, Leslie⁶⁷ found that the fraction boiling between 115 and 120°C and containing 2-methylheptane formed a glassy material at temperatures below -100°C. Crystallization and separation were successful in the presence of a methane-propane mixture.

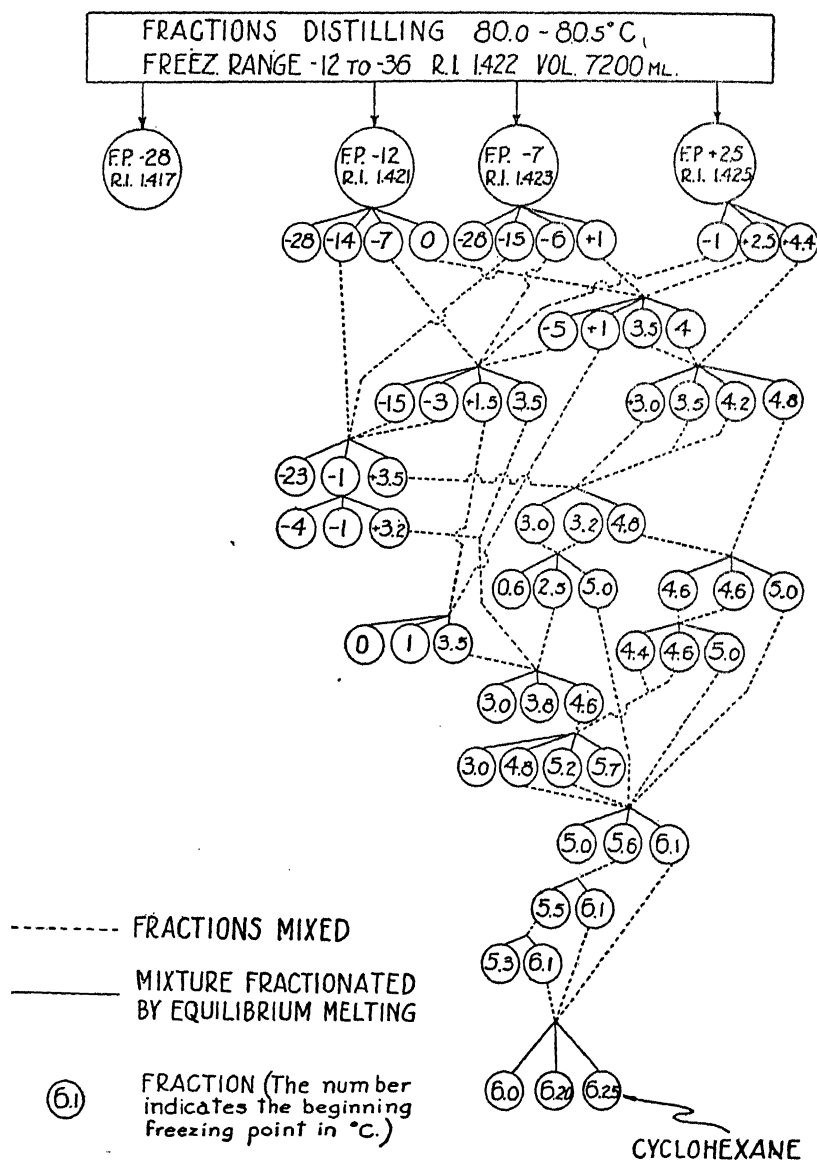


FIGURE 13. Isolation of cyclohexane by equilibrium melting. (Courtesy *Journal of Research of the National Bureau of Standards*)

Another fraction containing a nononaphthene (probably one of the dimethylethylcyclopentanes) became highly viscous and semi-solid at -143°C . In the presence of 1 volume of propane and 2 volumes of methane, the fraction (1 volume) was crystallized and separated into crystals and mother liquid. The mother liquid was blended with an

equal volume of dichlorodifluoromethane and fractionated by crystallization. Fractional distillation followed, and pure nononaphthene was formed.¹⁴⁰ Pure ethylcyclohexane was produced by fractional crystallization of the narrow cut, boiling from 131.5 to 132.5°C, with a propane-methane mixture (1 volume of the fraction, 2 volumes of propane, and 2 volumes of methane Rose and White¹⁰⁰).

An interesting example of the separation of three isomers of methyloctane by fractional distillation and crystallization has been described by White and Glasgow.¹³⁷ The boiling and melting points of these isomers are given in Table 23.

Table 23. Boiling and Melting Points of Isomeric Methyloctanes.

Hydrocarbon	Boiling Point at 760 mm (°C)	Melting Point (°C)
2-Methyloctane	143.25	-80.5
3-Methyloctane	144.18	-108.0
4-Methyloctane	142.43	-119.1

The narrow cut, boiling between 140.5 and 146°C and containing these isomers, was freed from aromatics and fractionated by distillation. The fractions obtained were systematically crystallized from solution in dichlorodifluoromethane; 2-methyloctane, having the highest melting temperature, was separated and purified by fractional distillation. The mother liquids boiling above 143.6°C with appropriate fractions boiling up to 144.4°C were systematically redistilled. The distillates boiling above 144.1°C were also crystallized from solutions in dichlorodifluoromethane and yielded 3-methyloctane. The low-boiling fractions from the fractional crystallization of 2-methyloctane were separated by distillation. The portions boiling between 142 and 143°C were azeotropically distilled with acetic acid and further fractionated by distillation to produce the portion boiling between 142 and 143.0°C. When fractionated by crystallization this gave pure 4-methyloctane.

Separation by Solvent Treatment

Solvent treatment of petroleum oils was one of the earlier methods of investigating their chemical composition. In the past this method was applied mostly to high-boiling fractions which cannot be separated by distillation without decomposition. Thus the method in question was considered as a substitute for distillation and was designated by Charitchkoff as "cold fractionation."

Charitchkoff²³ employed the method of Zaloziecky. He dissolved the residuum in amyl alcohol and precipitated the oil fractions with ethyl alcohol. The first fraction precipitated by a small amount of ethyl alcohol consisted of hydrocarbons of the highest specific gravity; an additional quantity of ethyl alcohol precipitated the second fraction, etc. The fractions were dissolved in ether and repeatedly precipitated with ethyl alcohol. Charitchkoff believed that the fractions finally obtained

were pure hydrocarbons. Actually they were very complex mixtures of many hydrocarbons.

Mabery⁷¹ separated heavy residues (after distillation up to 300°C at 30 mm pressure) by fractional precipitation with ether-alcohol mixtures. The empiric formulas were obtained for each fraction on the basis of ultimate analysis and molecular weights*. It is understood that the fractions produced also were complex hydrocarbon mixtures.

It is now fully recognized that separation of hydrocarbons by the solvent treatment cannot produce pure hydrocarbons, but can be successfully used for enrichment or partial separation of fractions comprised of hydrocarbons of different structures.

Solvent extraction is both similar to and essentially different from distillation. For instance, for the same series of hydrocarbons, for normal paraffins, solvent treatment would give the same results as distillation in view of the differing solubility of paraffins in the same solvent, which is affected by the molecular weight of the paraffins. The effect of molecular weight on solubility, however, is much less than that of chemical structure. Thus, a mixture of various hydrocarbons is separated by the solvent treatment mainly into fractions of different chemical structure. The effect of separation according to molecular sizes is much less. The best results are obtained with narrow fractions consisting of hydrocarbons of substantially the same molecular weight. An appropriate solvent separates such fractions into hydrocarbons of different chemical nature, as, for instance, aromatic and non-aromatic, etc. The method is extensively used for investigating the chemical composition of any fraction from gasoline to high-boiling lubricating or asphaltic fractions. The wide commercial application of the method is well known, but is completely beyond the scope of this volume.

As has been stated above, the separation of a chemically homogeneous product into fractions by solvents is carried out to a much lesser extent. Koch and Ibing,^{58*} for instance, treated (chloroform or ether) high molecular weight waxes with solvents. In this way the wax is separated into narrow fractions consisting of paraffins of various molecular weights. The fractionation of such waxes by distillation would be accompanied by decomposition.

The solvents employed for investigating the chemical composition of petroleum, as well as for commercial solvent treatment, are usually completely miscible with aromatic hydrocarbons, resinous components of petroleum, acids, bases, and sulfur compounds. The solubility of naphthenes and paraffins in such solvents is only insignificant, at least at low or moderate temperatures. Unsaturated hydrocarbons are intermediate

*It should be mentioned that the data of the ultimate analysis for many fractions separated by Mabery do not agree with other similar data. Fractions H of Mabery should contain a great proportion of resins and asphaltenes, so that the ultimate composition would show an appreciable content of oxygen. The sum of carbon and hydrogen should be much lower than 100 per cent. Actually, in all fractions the sum of carbon and hydrogen, determined by Mabery, was about 100 per cent, the deviations being no more than 0.1 per cent.

between aromatics and paraffins (or naphthenes). As a result, a solvent taken in an appropriate amount extracts chiefly aromatic hydrocarbons and resins, and also sulfur compounds, acids and bases, if present. Some of the paraffins and naphthenes are also dissolved in the solvent, because of their partial solubility and because the aromatic hydrocarbons extracted by the solvent increase the solubility of the paraffins. The final success of the solvent separation depends upon the selectivity of the solvent, the temperature (which affects the selectivity also), the percentage of the solvent, and the number of stages in batch operation or their equivalent in the continuous process.

The extract contains the solvent and extracted aromatics, as well as other hydrocarbons and compounds. Separation of the solvent from the extracted hydrocarbons must be complete. Distillation is a universal method of separation, if the difference in the boiling points of the hydrocarbons and the solvent is sufficient to make it possible. Liquid sulfur dioxide, for instance, can be easily distilled off from aromatic hydrocarbons extracted from various petroleum fractions, including gasolines. Such solvents as furfural and nitrobenzene can be separated by distillation from low-boiling gasoline fractions or high-boiling lubricating cuts. Other methods of separating the solvent are sometimes used to advantage. Thus, aniline and similar basic solvents can be separated by treatment with acids. Such solvents as methyl and ethyl alcohols are removed by dilution with water, if distillation is not feasible. A certain proportion of the solvent remains in the raffinate (naphthenic and paraffinic part of the original product) and must be removed by the same methods.

Low molecular weight alcohols, acetone, aniline, nitrobenzene, methyl cyanide, and liquid sulfur dioxide are chiefly employed for the separation of aromatics and resins from other classes of hydrocarbons in laboratory practice. Liquid sulfur dioxide is one of the most selective solvents for this purpose. For the extraction of high molecular weight aromatics, which are difficultly soluble in liquid sulfur dioxide, a certain proportion of benzene or toluene is added to the sulfur dioxide to increase its solvent power. On the contrary, a certain percentage of water (from 1 to 1.5 per cent) is frequently added to such solvents as acetone and methyl cyanide to decrease the solubility of non-aromatic components in the solvents.

Even partial separation of olefins from naphthenes and paraffins, as well as of naphthenes from paraffins, by solvent treatment is not easy because of the much smaller difference in solubility between these hydrocarbons. Indeed it is impracticable in most cases.

The number of more recent investigations of solvent extraction for separation of aromatic hydrocarbons is too great to be cited in this volume. The investigations of The National Bureau of Standards will be discussed briefly.

Solvent extraction can be combined with fractionation and separation of the solvent from the raffinate. In this case (extractive distillation) the solvent is introduced into the upper part of a fractionating column,

falling by gravity countercurrently to ascending vapors and extracting aromatic hydrocarbons on each plate. The solvent has a much higher boiling point than the hydrocarbons to be separated. Thus, the vapors are free or almost free of the solvent. Extractive distillation is similar to azeotropic distillation. Because of the great difference in the boiling points of the solvent and hydrocarbons, however, no azeotropic mixtures are formed in the extractive distillation.

Procedure of Extraction

There are various laboratory apparatus for extraction with solvents in a batch or continuous operation. Leslie⁶⁰ described two pieces of continuous counter-current flow apparatus for extraction with sulfur dioxide at atmospheric and elevated pressures, which were used by the Bureau of Standards. The apparatus with reflux has been described by Hersh, *et al.*,⁶¹ Cannon and Fenske,²⁰ Fenske and Hersh,⁵⁸ and others.

Extraction with reflux is performed in brief as follows (Fig. 14). If the solvent is lighter than the oil to be extracted, it is pumped continu-

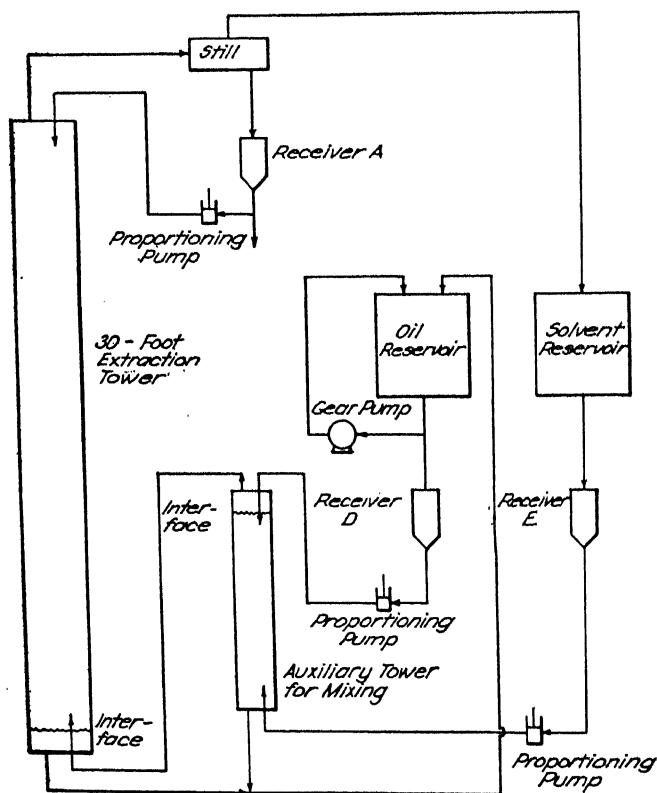


FIGURE 14. Continuous solvent treatment with recycling. (Courtesy Industrial and Engineering Chemistry)

ously into the bottom of the column containing the oil. The charging stock may be pumped from a charging tank to the top of the column. The solvent rises through the column to the top, dissolves gradually and preferentially the aromatic hydrocarbons, and finally discharges from the top into a still, in which the solvent is stripped from the oil components extracted. The regenerated solvent is pumped back to the bottom of the column, whereas the oil extracted is refluxed to the top. If the total oil extracted is returned, the operation is known as total reflux extraction. Otherwise, part of the extracted oil is withdrawn as a product and part of it is refluxed. The refined oil from the bottom of the column passes to the charging tank and also is refluxed, totally or partially, to the bottom of the column. It is more advantageous, however, to use an auxiliary or leaching tower for mixing the solvent with the oil to be treated; in this way the mixing of the solvent and charge (or refluxed refined oil) takes place in the auxiliary tower, and the solvent enters the fractionating tower saturated with extracted components of the charge. The regenerated solvent and the oil from the bottom of the main tower enter the auxiliary tower.

The extraction columns with reflux are similar to the familiar fractionating columns. Columns of the bubble-cap or packed type may be used for extraction, as well as empty columns of the spray type. It should be pointed out, however, that extraction columns are much less efficient than fractionating columns (*i.e.*, distillation). While the H.E.T.P. of laboratory fractionating columns may be as low as one inch or less, the height of the extraction columns equivalent to one equilibrium-batch operation averages from 3 to 10 feet. The reason for such a difference is due partially to the comparatively high viscosities of liquids at the temperatures of extraction, which prevent intimate contact between the two liquids and favor channelling. In addition to this, the high degree of dispersion of the two liquids causes the formation of stable emulsions and poor separation, preventing normal operation of the column.

Extraction of Low-boiling Fractions

White and Rose¹³⁰ extracted by liquid sulfur dioxide 40 liters of the distillate, boiling between 127 and 141°C, at an average temperature of -35°C. About 9 liters of extract and 31 liters of raffinate were obtained. Fig. 15 represents graphically the results of the extraction. It can be seen that the cuts produced from the extract and raffinate showed a great difference in aromaticity (refractive index), indicating the degree of separation of aromatics by the solvent treatment. The second treatment of the raffinate with the same solvent gave a very small additional amount of extract. The extract contained isomeric xylenes and ethylbenzene. The immiscible part, or raffinate, however, contained about 2 mole per cent of aromatics which were not extracted with liquid sulfur dioxide. Thus, as separation of aromatics by the solvent treatment is not quantitative, some additional treatment must be used for complete removal of aro-

matics. As will be seen later, adsorption or chemical methods (nitration or sulfurization) are satisfactory for this purpose.

The separation of aromatics from the fractions containing trimethylbenzenes was carried out by Mair and Schicktz.⁷³ The 40-liter fraction was extracted with liquid sulfur dioxide at -35 to -50°C . The extract totaled 9,537 cc. Various fractions of the extract had a refractive index

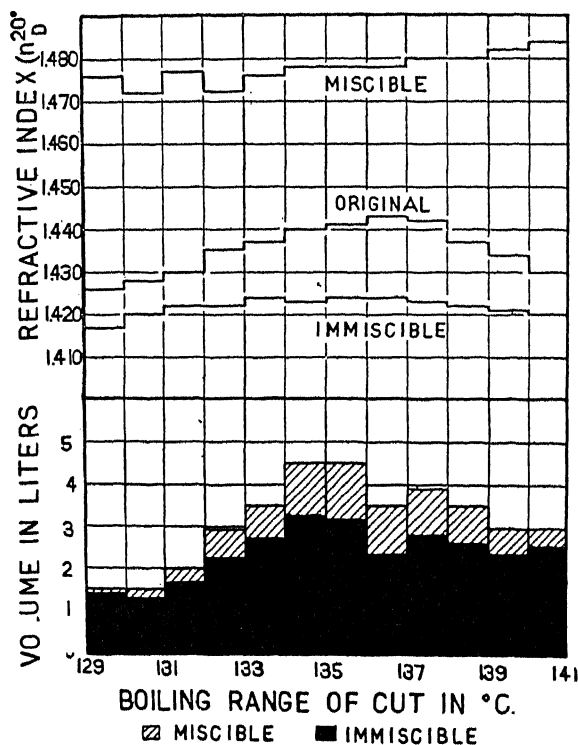


FIGURE 15. Change in volume and refractive index of distillation fractions upon extraction with liquid sulfur dioxide. (Courtesy *Journal of Research of the National Bureau of Standards*)

from 1.456 to 1.5116, i.e., were of high aromaticity. The separation of aromatics, however, was not complete, as in the previous case, and the raffinate contained a certain proportion of aromatics not removed by the treatment. The reaction of the raffinate with 100 per cent sulfuric acid (1 volume per $\frac{1}{4}$ volume of sulfuric acid) for 22 hours at room temperature resulted in sulfonation of the aromatic hydrocarbons left after solvent extraction. The sulfonic-acid layer was run into ice, and the sulfonic acids obtained were hydrolyzed into hydrocarbons (Chapter 3). A total of 1,030 cc of aromatic hydrocarbons were obtained by this way from the raffinate, i.e., about 11 per cent of aromatics was removed by the sulfonation.

Mair and Streiff⁷⁶ used two solvents for extraction of aromatic hydrocarbons from a kerosene fraction. Methyl cyanide, which appears to be of about the same selectivity for aromatics as does sulfur dioxide, was employed as a solvent. The advantage of this is that the process can be performed at room temperature. The extract contained aromatics and an appreciable amount of paraffins and naphthenes. The extract, including the solvent, was then treated with another solvent, Marcol, which is a commercial aromatic-free mixture of high-boiling paraffins and naphthenes having an initial boiling point of about 230°C at 56 mm of mercury. This second treatment produced pure aromatic hydrocarbons at the expense of certain losses of aromatics dissolved in Marcol, together with paraffins and naphthenes extracted by Marcol. The kerosene hydrocarbons were distilled from the Marcol and recirculated in the solvent treatment. The raffinate, or the portion immiscible with methyl cyanide, contained about 2½ per cent of aromatic hydrocarbons.

Extraction of Lubricating Fractions

Application of the solvent separation to lubricating-oil fractions has been discussed by Rossini,¹⁰³ Mair and Schickanz⁷⁴ and Mair and Willingham.⁷⁸ A lubricating stock was first dewaxed at -18°C in ethylene chloride solution to separate a "wax" portion, which was 35 per cent of the initial product. The remainder was then treated at about 40°C with liquid sulfur dioxide. As a result, 21 per cent of extract was separated from 44 per cent of raffinate (per cents are with respect to the initial lubricating product). The extract was treated at -55°C with petroleum ether, producing a petroleum-ether soluble portion (13 per cent) and an asphaltic portion insoluble in ether (8 per cent).^{*} The raffinate was subjected to adsorption by silica gel, which retained 9 per cent of the more aromatic material and left 35 per cent of the water-white oil portion (per cent based on the original stock). The silica gel hold-up was combined with the petroleum-ether soluble portion and formed the "extract" portion, totaling 22 per cent of the initial lubricating stock. Thus the final results are as follows:

Water-white portion	35 per cent
Extract	22 " "
Asphalt	8 " "
Wax	35 " "

This preliminary solvent treatment of the original lubricating stock gave a rough separation of the components. The wax and water-white portions consisted mostly of paraffinic and naphthenic hydrocarbons; no oxygen compounds were present in significant amounts. The extract portion consisted chiefly of aromatic hydrocarbons and also of some oxygen-sulfur compounds. This portion contained about 0.9 per cent sulfur, 0.1 per cent nitrogen, and 0.5 per cent oxygen, corresponding to about 0.1, 0.03, and 0.1 atom of sulfur, nitrogen and oxygen, respectively, in a mole-

^{*}See Chapter 4.

cule containing about 65 carbon and hydrogen atoms. The asphaltic portion contained a large part of all the sulfur, nitrogen and oxygen compounds in the original lubricating stock.

This preliminary rough separation by solvents was followed by fractionation and subsequent solvent treatment of narrow fractions produced from the water-white and extract portions. The water-white portion was distilled under high vacuum to produce numerous substantially constant-boiling fractions, which, however, consisted of various hydrocarbons of different chemical nature. The following solvent treatment separated these constant-boiling fractions into subfractions of different solubility, *i.e.*, of different aromaticity or naphthenicity. Some fractions were separated each into 25-35 subfractions by extraction with acetone containing 1½ per cent of water. The extraction was performed in 46-foot columns with reflux. The extract portion was distilled in the same manner, and some fractions produced were treated with methyl cyanide (plus some acetone for the less soluble fractions), giving each from 30 to 40 subfractions. Acetone could not be used for solvent-treating the extract portion because of the high solubility of the aromatic oil in this solvent. Each of the "final" fractions, produced from either the water-white or the extract portion, is still far from being a pure component, but is more nearly so than any other material separated from lubricating oils.

The application of solvent treatment to the separation of narrow fractions of lubricating oils also was described by Cannon and Fenske²⁰ and Fenske and Hersh.³⁸

The use of low molecular weight paraffins, such as liquid propane, butanes, pentanes etc., as solvents and precipitating agents will be described in Chapter 9.

Adsorption and Desorption

This section is confined to the adsorption of hydrocarbons by various adsorbents. The removal of sulfur and oxygen compounds by adsorption will be discussed in Chapter 8. Such adsorbents as clay and bauxite are widely used commercially for this purpose.

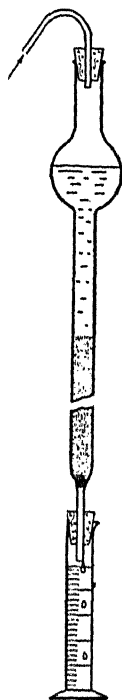
The selective adsorption of certain hydrocarbons, not being a commercial process, can be successfully applied in many cases for separation of hydrocarbon mixtures.

A possibility of separating aromatic hydrocarbons from others by adsorption has been demonstrated by Day,²⁷ Tarassov,¹¹⁵ Grimm, Randenbusch and Wolff,⁴⁵ and Hofmeier and Meiner.⁵⁸ The members of the National Bureau of Standards investigated and systematically applied the adsorption of aromatics by silica gel for separation.

Mair and White⁷⁷ described a simple method and apparatus for fractional adsorption. The apparatus consists of glass tubes mounted vertically and filled with silica gel (Fig. 16). The tubes are 40 cm long and 1.5-1.7 cm inside diameter. The height of the silica gel is from 36 to 40 cm (50 grams). The top part of the tube is a sealed glass bulb which

serves as a reservoir for the hydrocarbon mixture. To the top of the bulb a rubber tube is attached for the application of air pressure during filtration. The pressure is about 4 lbs/sq inch. The time of filtration varies from 16 to 48 hours depending upon the tightness of the packing. Two grades of silica gel were used: coarse, 40- to 200-mesh, and fine, 200-mesh or more. The reactivation of silica gel by oxidation was performed at a temperature of 300 to 350°C with an apparently complete restoration of activity. The charge of hydrocarbons was 100 cc.

FIGURE 16. Adsorption tube.
(Courtesy *Journal of Research of
the National Bureau of Stand-
ards*)



When all the filtrate was drained, the hydrocarbon fractions retained by silica gel were displaced by adding water at the top of the tube. An additional amount of hydrocarbons was obtained after the silica gel had been transferred with more water from the apparatus to a 500-cc Erlenmeyer flask. Finally, the last portion of hydrocarbons was recovered by vigorous shaking of silica gel in the Erlenmeyer flask with water. The total recovery was from 97 to about 100 per cent.

The filtration of the mixtures of normal paraffins (normal octane and decane) with aromatics (mesitylene and meta-xylene), as well as of methylcyclohexane with aromatics (toluene and benzene), was studied. Mixtures consisting of 97 cc of a paraffin or naphthene and 5 cc of an aromatic were used. The refractive index of the various fractions produced after the filtration was determined for calculation of aromatic

content. The filtrates and the main portions displaced by water were pure paraffins and naphthenes. The two portions last extracted with water were the concentrates of the aromatic used. On the average, from 97 cc of a paraffin (or naphthene) and 5 cc of an aromatic more than 90 cc of the pure paraffin and from 5 to 8 cc of the aromatic concentrate were recovered. When 92 cc of a paraffin and 10 cc of an aromatic were used, 55 to 60 cc of a pure paraffin and a correspondingly larger amount of the aromatic concentrate were obtained. Thus, the effect of separation depends upon the concentration of aromatics at the same relative amount of silica gel. If the concentration of aromatics is higher than 15 per cent, preliminary extraction with sulfur dioxide or other appropriate solvent is recommended.

The experiments described show clearly that the separation of aromatics from paraffins or naphthenes by adsorption is much more complete than by solvents. This conclusion seems to be in line with the much more selective action of large active surfaces as compared with the physical action of solvents.

The separation of an olefin (diamylene) from a paraffin can also be effected, but less completely than in the case of aromatic hydrocarbons. Experiments on the separation of a naphthene from a paraffin showed that the separation is "disappointingly small." It has been proved, however, that naphthenes tend to be adsorbed by silica gel to a somewhat greater extent than paraffins. According to the authors, "the separation of naphthenes from paraffins is frequently so difficult that a method which gives any separation whatsoever is worthy of consideration as a research tool."

The same authors applied adsorption by silica gel to the separation of aromatics from a fraction boiling between 140 and 145.5°C from which the aromatics were first removed by extraction with sulfur dioxide. Thus the fraction consisted predominantly of paraffins (isononanes) and some naphthenes. The adsorption columns were about 50 cm long and 2 or 3 cm wide. The charge of silica gel was 100 or 200 grams, and the time of filtration about 20 minutes. The distillate was separated into three fractions, each of which was treated with coarse silica gel. The results are given in Table 24.

Table 24. Volumes and Refractive Indices of Fractions Before and After Filtering Through Silica Gel.

Boiling Range Before Filtration (°C, 760 mm)	Volume (cc)				Refractive Index $n_{D_{20}}^{\circ}$		
	Before Filtering	After Filtering Filtrate	Adsorbed	Lost	Before Filtering	After Filtering Filtrate	Adsorbed
140-142.5	5,230	4,950	210	115	1.415	1.4125	1.445
142.5-144	5,850	5,380	360	110	1.4125	1.4115	1.425
144-145.5	5,660	5,150	460	50	1.418	1.416	1.438

The separation of aromatic hydrocarbons is rather sharp.

Another example of the separation of aromatics by silica gel has been given by Mair and Streiff.⁷⁸ A kerosene fraction, having been treated

with sulfur dioxide, contained about $2\frac{1}{2}$ per cent of aromatics. This fraction in the amount of two liters was separated by treatment with silica gel into a filtrate (approximately 1,700 cc) and an adsorbed oil (300 cc). The filtrate was completely free of aromatics, whereas the adsorbed part contained about 20 per cent of aromatic hydrocarbons.

The application of adsorption to the separation of aromatics from high-boiling fractions was not as wide as in the case of light fractions. Mair, Schiektanz and Rose⁷⁶ used silica gel for removing aromatic hydrocarbons and sulfur compounds from a lubricating Mid-Continent stock. They also proved that the adsorption does not affect the structure or properties of the compounds adsorbed.

Barrer⁸ claims that certain zeolites adsorb mostly straight-chain paraffins as compared with isoparaffins and cyclic hydrocarbons.

In recent publications Barrer and Ibbitson^{6a} reported on the experiments and theory of the adsorption or occlusion of hydrocarbons by chabazite and active analcite. The occlusion is a function of the cross-sectional diameter of hydrocarbon molecules. Molecules with a cross-sectional diameter equal to 4.89 Å (normal paraffins) or less (methane, ethane) are occluded by the above zeolites, whereas those with a cross-sectional diameter equal to or greater than 5.58 Å (isoparaffins and aromatic hydrocarbons) are totally excluded. The rate of occlusion, however, decreases as the chain-length of normal paraffins increases. These findings apparently open the door to some analytical and perhaps practical possibilities along the line of separation of normal paraffins from isomers.

In the recent paper by Rossini *et al.*,¹⁰⁶ the authors described a much wider application of the adsorption method to the separation of hydrocarbons. Naphtha or gasoline is separated quantitatively by the adsorption into two portions: aromatic and naphthene-paraffinic. The small amount of non-hydrocarbon constituents (mostly sulfur compounds) is associated with the aromatic portion and is separated by further adsorption to yield the pure aromatic portion. The aromatic and non-aromatic portions are then fractionated separately. The aromatic part contains a limited number of hydrocarbons, boiling in the range of gasolines, and can be resolved into individual aromatics without difficulty. In addition to this, fractionation of the naphthene-paraffinic fraction is greatly improved, because aromatic hydrocarbons do not interfere with the fractionation of paraffins and naphthenes.

In a later publication Mair and Forziati^{71a} described a modification of the separation of hydrocarbons retained and adsorbed by the adsorbent. The paraffins and naphthenes retained by the adsorbent are displaced by adding a low-boiling hydrocarbon, *e.g.*, normal pentane. The aromatics adsorbed are desorbed by methyl alcohol which may be removed by extraction with water.

The same authors^{71b} applied a simple method for determining the amount of aromatics in gasolines by adsorption. The gasoline is filtered

through a column of an adsorbent producing an aromatic-free filtrate, the amount of which depends upon the original concentration of aromatics in the gasoline. A "calibration curve" is determined experimentally for a given gasoline, plotting the amount of aromatic-free filtrate versus the concentration of aromatic hydrocarbons in the gasoline.

Alibone¹ separated large fractions and products, such as dewaxed paraffin distillate or bright stock into a series of fractions adsorbed with silica gel. The product in the amount of 50 grams is dissolved in 500 cc of aromatic-free petroleum ether (boiling range from 60 to 80°C) and filtered through 300 grams of silica gel in a column having a length: diameter ratio of about 15:1. Fractions (100 cc) of filtrate are collected and then fresh petroleum ether is added to wash the silica gel and to produce more fractions. The fractions are stripped in a carbon dioxide current to remove petroleum ether. Then the column is drained completely and dried. The dried silica gel is removed and also divided into several portions, which are extracted separately in a Soxhlet apparatus with methylethylketone. By this method, a dewaxed pressed distillate (sp. gr. 0.927) was separated into 12 fractions of specific gravity from 0.867 to 1.087; or a Pennsylvania bright stock, sp. gr. 0.891, into 12 fractions of specific gravity from 0.863 to 1.001. Other adsorbents, such as bauxite and bleaching earths, can also be used, but the effect of separation with these adsorbents is less than with silica gel. The method of adsorption undoubtedly will find a wider application to the separation of certain petroleum hydrocarbons than it has had up to the present.

The desorption method described in Chapter 1 can be applied to the analysis of liquid fractions and products. The hydrocarbons are adsorbed by silica gel, using about 10 grams per one gram of the product. The desorption takes place at temperatures up to 200-300°C. The rate of desorption must be slow, *e.g.*, 0.2 gram of hydrocarbons per hour from 100 grams silica gel with 10 grams adsorbed hydrocarbons. By this method the separation of normal hexane from cyclohexane is fairly sharp, while the separation of aromatic hydrocarbons from paraffins and naphthenes is practically quantitative. The literature on the desorption method has been given in Chapter 1.

Aniline Points

The method of aniline points (or similar points for other solvents) is very close to the method of solvent extraction described above. This method is also based upon the difference in the solubility of various hydrocarbons in polar solvents, such as aniline, nitrobenzene, etc.

Whereas treatment by a solvent separates the product into two parts, one of which is soluble and the other is insoluble in the solvent, the temperature of complete miscibility of the solvent and the product is determined by the method of aniline and similar points. Accordingly, hydrocarbons easily soluble, *e.g.*, in aniline, will have a low aniline point, and *vice versa*. The aniline point is a quantitative measure of the solubility

of a hydrocarbon or a fraction in aniline. In this sense, the aniline point can be classified as one of the physical properties of hydrocarbons.

Many physical properties of hydrocarbons distilling in the same boiling range differ substantially for various classes of the hydrocarbons. The values of specific gravity and refractive index are highest for aromatics, intermediate for naphthenes, and lowest for paraffins. The aniline points and similar constants of solubility in organic solvents have the opposite trend, being lowest for aromatics and highest for paraffins. In many cases the specific gravity, refractive index, or aniline point of certain fractions may be used for an approximate calculation of the chemical composition. Either method under appropriate conditions may give reliable results. Aniline points are used very extensively because of the simplicity of the operations involved.

The methods in question can be applied to rather narrow fractions, if the average physical constants (*i.e.*, specific gravity, refractive index, or aniline point) or paraffins, naphthenes and aromatics boiling in the range of the narrow fractions are known. As will be seen later, the values of the physical properties of mixtures have approximately a linear relationship versus the composition.

The aniline point is the critical temperature of the solubility of a substance in aniline, *i.e.*, the temperature of its complete miscibility with aniline. If the aniline point is determined for equal volumes of the product and aniline, the procedure is as follows:

Five cc of the product and 5 cc of freshly distilled aniline are placed in a test-tube (25 mm in diameter and 150 mm long) provided with a glass stirrer or a solid wire, as well as with a thermometer. The test-tube is fixed in a wider tube, which acts as an air jacket, and is heated in a glass of water. The aniline point is determined as the temperature of complete miscibility of aniline and product, or as the temperature of separation of two phases from the homogeneous mixture. The first determination is made on heating two layers of aniline and product; the second is made on cooling the homogeneous mixture of aniline and product obtained above the critical temperature.

The aniline point determined by this method may differ from the "true" critical temperature, above which any mixture of the product and aniline is homogeneous. The determination of the true critical temperature is carried out as follows. To 5 cc of the product 3 cc of aniline are added, and the temperature of complete miscibility is determined. The method is the same as previously described. Then 0.5 cc of aniline is added to the mixture, and the temperature of complete miscibility of 5 cc of the product and 3.5 cc of aniline is determined. The temperature is somewhat higher than that found in the first determination. This procedure, *i.e.*, adding 0.5 cc of aniline, is repeated until the maximum temperature is reached, which corresponds to the true critical temperature of solubility of the product and aniline.

The difference between the aniline point at equal volumes of product

and aniline (or the "aniline point," as it will be specified) and the true critical solubility temperature (or the "maximum aniline point," as it will be called) for petroleum fractions is usually not great; it depends upon the content of aromatics and the boiling point of the fractions. The aniline point and the maximum aniline point of fractions freed of aromatics are practically identical, particularly for fractions boiling below 300°C. The difference does not exceed 0.2°-0.3°C. Thus, for such fractions, the aniline points and maximum aniline points may be used indiscriminately.

If the proportion of aromatics in a fraction does not exceed 5 per cent, the aniline point and the maximum aniline point again are about equal, particularly for low-boiling fractions. The maximum aniline point, however, may be higher by 5°-7°C than the aniline point for highly aromatic and high-boiling fractions.

It is understood that any calculations based on aniline points should be made for aniline values determined by the same method, *i.e.*, by using either equal volumes of the product and aniline, or maximum aniline points. As pointed out above, however, the aniline points and the maximum aniline points of aromatic-free fractions or fractions poor in aromatics (less than 5 per cent), boiling below 300°C, are practically identical. Aniline points are more widely used than maximum aniline points because the procedure is simpler.

The methods described can be applied only to light oils or distillates not darker than No. 8 ASTM Color. The method of determining the aniline points of dark oils has been described by Donn,⁸¹ Van Wijk and Boelhouwer,¹²⁵ Matteson, Zeitfuchs and Eldredge⁸⁰ and Williams and Dean.^{140b} It should be kept in mind, however, that the aniline points of dark oils, usually consisting of substances of broad boiling range, cannot be used for any analytical calculations.

The purity of aniline is an important prerequisite for satisfactory results. The presence of moisture is particularly important. Ormandy and Craven⁸⁸ give the following changes in the aniline points of heptane and cyclohexane, depending on the amount of water in the aniline:

	Content of Water		
	0.07%	1.02%	1.75%
Aniline point of heptane	68.4°C	74.3°C	80.0°C
" " " cyclohexane	29.2	34.5	39.3

A content of 1 per cent water in aniline increases the aniline point by 5° to 6°C. In determining the content of aromatics quantitatively by the difference in aniline points, the moisture content may be disregarded; but in the determination of naphthenes and paraffins, where it is necessary to know the absolute aniline point, the amount of moisture in the aniline is of great importance.

It should be understood that aniline is only one of many solvents which can be used for the method in question. Aniline is preferred be-

cause of its availability, purity and convenience in operation; the aniline points of petroleum fractions lie mostly between 0° and 120°C. Nitrobenzene can also be used successfully, particularly for low-boiling fractions. The aniline points of low-boiling fractions may be too high to prevent evaporation under atmospheric pressure, while the nitrobenzene points of such fractions are in the neighborhood of room temperature or lower (Erskine³⁴). Orthotoluidine also gives much lower critical points than does aniline (Carpenter³¹). Furfural was recommended by Rice and Lieber.³² Recently nitrobenzene and chlorex points have been determined by Woodburn *et al.*^{137b}

The aniline points of hydrocarbons belonging to the same class as well as those of petroleum fractions of the same crude, increase with increasing molecular weight or boiling temperature. For paraffins the aniline points increase from 70°C for normal heptane to about 125°C for

Table 25. Maximum Aniline Points of Pure Hydrocarbons.

Hydrocarbon	Aniline Point (°C)	Hydrocarbon	Aniline Point (°C)
<i>Paraffins</i>		<i>Unsaturates</i>	
Butane	84.0	Pentene-1	19.3
Isobutane	109.0	Hexene-1	22.9
.....		Hexene-2	26.0
<i>n</i> -Pentane	71.4	Hexene-3	27.0
2-Methylbutane	77.8	Heptene-1	26.6
.....		Octene-1	32.8
<i>n</i> -Hexane	69.0	Nonene-1	38.6
2-Methylpentane	74.7	Decene-1	45.6
3-Methylpentane	69.4	Hexadecene-1 (cetene)	72.0
2,2-Dimethylbutane	80.7	Cyclopentene	< -10
2,3-Dimethylbutane	72.3	Cyclohexene	-20
.....		<i>Naphthenes</i>	
<i>n</i> -Heptane	70.0	Cyclopentane	18.0
2-Methylhexane	73.8	Methylcyclopentane	35.0
3-Methylhexane	70.5	Ethylcyclopentane	38.5
3-Ethylpentane	66.3	Dimethylcyclopentanes isomers	45-48
2,2-Dimethylpentane	78.0	Propylcyclopentane	45.0
2,3-Dimethylpentane	68.1	Butylcyclopentane	50.0
2,4-Dimethylpentane	78.8	Cyclohexane	31.0
3,3-Dimethylpentane	69.7	Methylcyclohexane	41.0
2,2,3-Trimethylbutane	72.3	Ethylcyclohexane	43.8
.....		Dimethylcyclohexanes isomers	42-49
<i>n</i> -Octane	71.8	Propylcyclohexane	49.8
Methylheptanes isom	71-74	Butylcyclohexane	54.4
Dimethylhexanes isom	70-77	Decalin	33.6
Trimethylpentanes isom	67-79	<i>Aromatics</i>	
.....		Benzene	< -30
<i>n</i> -Nonane	74.5	Toluene	do
Nonanes isom	71-81	Ethylbenzene	do
.....		Xylenes	do
<i>n</i> -Decane	77.5	Propylbenzene	do
<i>n</i> -Pentadecane	92.0	Butylbenzene	do
<i>n</i> -Eicosane	105.0	Decylbenzene	-0.6
<i>n</i> -Triacontane	125.0	Cetylbenzene	40.4
		Tetralin	< -20
		Methylnaphthalenes	< -30

normal C₃₀H₆₂. Exceptions to this are *n*-butane and *n*-pentane, which have somewhat higher aniline point values. Isoparaffins usually have

higher aniline points than normal paraffins of the same molecular weight, but this difference is not very considerable, particularly as compared with the difference between paraffins and naphthenes. For instance, the aniline point of normal heptane is 70°C and that of isomeric heptanes varies from 66° to 79°C.

The aniline points of naphthenes are much lower than those of paraffins of the same boiling range. Those of cyclopentane and cyclohexane are 17° and 30.5°C, respectively. The aniline points of the derivatives of these naphthenes are correspondingly higher, but the average difference between the aniline points of paraffins and monocyclic naphthenes of the same boiling range is from 35 to 20°C depending on the molecular weight. Polycyclic naphthenes, such as decahydronaphthalene and its derivatives, have much lower aniline points than monocyclic naphthenes of the same boiling range. Olefins, aliphatic and cyclic, have aniline points somewhat lower than monocyclic naphthenes of the same boiling range. Aromatics have the lowest aniline points. Table 25 summarizes the maximum aniline points of various hydrocarbons.

Ball^{2a} developed the "aniline function":

$$\frac{\text{Max Anil Point (°K)}}{\text{Boil Point (°K)}} \times \text{Mol Wt}$$

in which the maximum aniline point and boiling point of hydrocarbons are expressed in degrees Kelvin. The aniline function is additive for hydrocarbons of each homologous series. As a result, the aniline function and therefore the aniline point may be calculated with the aid of a few constants which characterize the hydrocarbon series and the increment almost independent of the series.

Determination of Aromatics by Aniline Points

The fractions of crudes for the determination of aniline points or maximum aniline points are distilled mostly in the range of 50°C. However, low-boiling fractions are distilled according to the distillation range of low molecular weight aromatic hydrocarbons. Thus, the distillation of crudes produces the following fractions:

Benzene fraction, 60°-90°C

Toluene fraction, 90°-122°C

Xylenes and ethyl benzene fraction, 122°-150°C, 150°-200°C, and so forth.

The high-boiling fractions above 250°C are distilled in a vacuum to avoid decomposition. The conversion of the boiling points at reduced pressures to the atmospheric pressure may be made, *e.g.*, by the chart given by Beal and Docksey.⁹

This method is applied to straight-run distillates only. Cracked distillates, containing unsaturates, cannot be analyzed successfully by the method in question, since unsaturates have about the same aniline

points as naphthenes. In addition, the unsaturates, unlike aromatic hydrocarbons, cannot be removed selectively and quantitatively.

The determination of aromatics in petroleum fractions by the aniline method gives the most reliable results because of the very low aniline points of aromatics. Accordingly, there is a wide variation in the aniline points before and after the removal of aromatics. Thus, the percentage of aromatics in a petroleum fraction, X , is calculated on the basis of the depression of aniline point effected by aromatics present in this fraction:

$$X = K(T_2 - T_1),$$

where T_1 and T_2 represent, respectively, the aniline points of the fraction before and after the removal of aromatics, and K the coefficient or the percentage of aromatics (by weight) effecting 1°C of depression.

The coefficient K is determined experimentally for each fraction. Its value may depend upon the nature of aromatic hydrocarbons, their concentration, and the nature of the fraction. The nature of aromatic hydrocarbons is of particular importance. As will be seen later, the value of the coefficient K varies from the benzene fraction to higher-boiling fractions, and is determined for various aromatics boiling in the range of a given fraction. However, as aromatic hydrocarbons boiling in the same range have about the same coefficients, a certain average coefficient may be determined for each fraction.

Tilicheyev and Dumskaya,¹¹⁰ for instance, obtained the following data on the coefficients for various xylenes and ethylbenzene dissolved (10 per cent) in an oil fraction distilling between 130° and 140°C :

<i>o</i> -xylene	1.26
<i>m</i> -xylene	1.28
<i>p</i> -xylene	1.28
ethylbenzene	1.30

Thus the average coefficient is close to 1.28. The maximum aniline points were determined in this case.

As mentioned above, an approximately linear relationship exists for the depression of aniline points versus the concentration of aromatics or other hydrocarbons causing the depression. Thus, the coefficients K are almost independent of the concentration, at least for concentrations of aromatics not exceeding 25-30 per cent by weight. The coefficient K gradually decreases with concentration for concentrations greater than 25-30 per cent. For this reason, it is best not to use the aniline method for concentrations of aromatics exceeding 25 per cent. If the concentration of aromatics in a fraction exceeds this limit, it should be diluted with the same fraction freed of aromatics to an appropriate concentration.

The same authors give the following data on the effect of the concentration of *m*-xylene upon the coefficient K for the fraction distilling between 122° and 150°C :

Concentration of <i>m</i> -xylene (% by weight)	Coefficient <i>K</i>
1	1.22
2	1.27
5.03	1.27
10.07	1.26
30.31	1.22
50.18	1.13
69.97	1.00

The maximum aniline points also were determined in this case.

The coefficients *K* depend on the chemical composition of the fraction, *i.e.*, not only on the boiling range but also on the origin of the fractions boiling in the same range. Table 26 includes some data of Tilicheyev and Dumskaya on this subject.

Table 26. Maximum Aniline Points and Aniline Coefficients of Toluene in Various Fractions.

Fraction	Max Aniline Point (°C)	Same with 10% Toluene	Coefficient <i>K</i>
105°-115°C, paraffin-base	60.30	52.23	1.25
95°-122°C, naphthenic base	50.62	42.23	1.21
95°-122°C, mixed base	54.71	46.44	1.25
Methylcyclohexane	40.50	31.84	1.16

From these data it is evident that the effect of the chemical nature of closely boiling fractions on the aniline coefficients is comparatively small, particularly for the fractions produced from various crude oils.

The method of determining the percentage of aromatic hydrocarbons by the aniline points is based on the complete removal of aromatics by treatment with strong sulfuric acid. The mechanism of this treatment is discussed in detail in Chapter 3. An approximate estimation of the aromatic content can be made on the basis of the decrease in the volume of a product after treatment with sulfuric acid. This method, however, is only approximate, because of the partial absorption of naphthenes and paraffins by the sludge formed.

As will be seen in Chapter 3, two or three volumes of 96-98 per cent sulfuric acid per volume of a straight-run fraction are sufficient for the quantitative removal of aromatics. The procedure is as follows: 100 cc of a fraction are mixed with three volumes of 98 per cent sulfuric acid and shaken for 30 minutes. After separation in a separatory funnel the fraction may be treated repeatedly with three volumes of sulfuric acid of the same concentration to insure complete removal of aromatics. In most cases this repeated treatment is not necessary. The treated fraction, after separation from the sludge, is neutralized, washed, and dried. The aniline points or maximum aniline points are determined before and after the treatment, and the percentage of aromatics is calculated by multiplying the depression of aniline point (*i.e.*, the difference between the aniline points before and after the treatment) by the aniline coefficient *K*.

High-boiling and viscous fractions are usually diluted with a non-

aromatic naphtha and then treated with concentrated sulfuric acid, as will be described in Chapter 3.

The aniline coefficients K were determined experimentally for various aromatic-free oil fractions by dissolution of aromatic hydrocarbons in weighed amounts. The low-boiling fractions, 60°-95°C, 95°-122°C and 122°-150°C, have been investigated thoroughly by many authors. The aniline coefficients for these fractions are determined with more accuracy than for high-boiling fractions. Table 27 contains the data on the aniline coefficients for these fractions.

Table 27. Aniline Coefficients for Low-boiling Fractions.

Fraction (°C)	Method of Maximum Aniline Points	Method of Aniline Points
Benzene, 60-95	1.15	1.19
Toluene, 95-122	1.23	1.20
Xylene, 122-150	1.28	1.23

Thus for low-boiling fractions both methods give very close values of the aniline coefficients.

The determination of the coefficients for high-boiling fractions, *i.e.*, 50°-fractions above 150°C, meets serious difficulties because of the large number of aromatics which may be in them. Carpenter²¹ determined the depression of aniline points effected by aromatics extracted from petroleum for various kerosene fractions of a crude. Table 28 gives the average values of the aniline coefficients calculated on the basis of Carpenter's data for concentrations of aromatics up to 30 per cent.

Table 28. Aniline Coefficients for Naphtha and Kerosene Fractions
(Method of Aniline Points).

Fraction (°C)	Aniline Coefficient
125-150	1.22
150-180	1.22
180-200	1.27
200-230	1.30
230-250	1.35
250-270	1.32

An extensive study of the maximum aniline coefficients for high-boiling fractions was carried out by Sachanen and Virobianz.^{100, 107} Aromatic hydrocarbons in varied concentrations from 5 to 70 per cent were dissolved in 50°-fractions (above 150°C) obtained from various crude oils to determine their depressing effect on the aniline point. In the fractions from 150 to 200°C the following hydrocarbons were dissolved: cymene, mesitylene, cumene, propylbenzene, and aromatic hydrocarbons separated from these fractions by liquid sulfur dioxide. The following hydrocarbons were investigated in the fractions from 200 to 250°C: naphthalene, methylnaphthalenes, tetralin, and aromatics extracted from these fractions. Diphenyl, diphenylmethane, 1,6-dimethylnaphthalene, and aromatics extracted from various fractions of the same boiling range were dissolved in the fractions from 250 to 300°C. Finally, in fractions

above 300°C only hydrocarbons extracted by sulfur dioxide were dissolved.

The effect of the nature of aromatic hydrocarbons, as well as of the origin of fractions (of the same boiling range), on the aniline coefficients is not too great, so that some average value can be found for each 50°-fraction. Table 29 gives the data on the aniline coefficient for the fraction from 200 to 250°C of various origins and for various aromatic hydrocarbons. As will be seen from the table, the variations of the coefficient at the same concentration of aromatics are comparatively small. The average value can be accepted as 1.68.

Table 29. Aniline Coefficients, K , for Fractions from 200° to 250°C.
(Concentration of aromatics 10 per cent by weight).

Fraction	Specific Gravity 15°/15°C	Aromatic Hydrocarbon	Aniline Coefficient
Naphthenic base	0.825	Naphthalene	1.77
" "	"	Methylnaphthalene	1.77
Mixed base	0.797	Aromatic extract	1.72
Paraffin base	0.791	Tetralin	1.61
" "	"	Aromatic extract	1.62
Asphaltic base	0.809	Methylnaphthalene	1.68
" "	"	Aromatic extract	1.72

The effect of the concentration of aromatics on the aniline coefficients is much more pronounced for high-boiling than for low-boiling fractions, i.e., those boiling up to 150°C. Thus, the authors have given both Table 30 and a curve (Fig. 17) for calculation of aniline coefficients for various fractions and concentrations of aromatics.

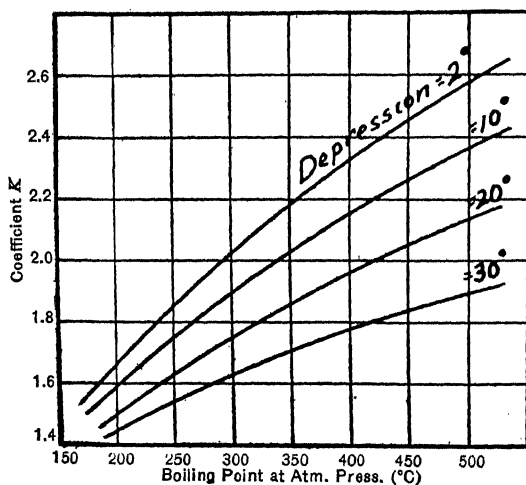


FIGURE 17. Coefficient K of petroleum fractions versus boiling point.

The determination of aromatics by the method of aniline points gives fairly reliable results for straight-run fractions. The average error in determination of the percentage of aromatics by this method is 7 per cent

(of the aromatic) for the fractions boiling up to 150°C, and 15 per cent for high-boiling fractions. It should be pointed out, however, that the figures obtained relate to the aromatic hydrocarbons which are removed by the treatment with sulfuric acid, *i.e.*, which are sulfonated under the conditions of the treatment. The question of how completely the aromatic hydrocarbons or the hydrocarbons containing aromatic rings are removed by this treatment will be discussed in detail in Chapter 3.

Table 30. Aniline Coefficients for Aromatics in Oil Fractions at Different Depressions.

Depression (°C)	Boiling Temperature of Fractions Coefficients							
	150-200°	200-250°	250-300°	300-350°	350-400°	400-450°	450-500°	500-550°
2	1.58	1.76	1.94	2.10	2.26	2.40	2.52	2.64
4	1.56	1.74	1.91	2.06	2.21	2.35	2.46	2.57
6	1.54	1.72	1.88	2.03	2.17	2.30	2.40	2.50
8	1.52	1.70	1.85	1.99	2.12	2.25	2.35	2.44
10	1.50	1.68	1.82	1.95	2.08	2.20	2.30	2.39
12	1.49	1.66	1.79	1.92	2.04	2.16	2.26	2.34
14	1.48	1.64	1.76	1.88	2.00	2.11	2.22	2.28
16	1.47	1.62	1.74	1.85	1.96	2.07	2.18	2.23
18	1.46	1.60	1.71	1.82	1.93	2.03	2.13	2.18
20	1.45	1.57	1.68	1.79	1.90	2.00	2.08	2.13
22	1.44	1.55	1.66	1.77	1.87	1.96	2.04	2.08
24	1.43	1.54	1.64	1.74	1.84	1.92	2.00	2.03
26	1.42	1.52	1.62	1.71	1.80	1.88	1.96	1.98
28	1.41	1.51	1.60	1.68	1.76	1.84	1.92	1.94
30	1.40	1.49	1.58	1.66	1.73	1.80	1.87	1.90
32	1.39	1.48	1.56	1.64	1.71	1.77	1.84	1.86
34	1.38	1.46	1.54	1.62	1.68	1.74	1.80	1.82
36	1.37	1.45	1.52	1.59	1.65	1.71	1.76	1.78
38	1.36	1.43	1.50	1.57	1.62	1.67	1.72	1.74
40	1.35	1.42	1.48	1.54	1.59	1.64	1.68	1.70
42	1.34	1.40	1.46	1.51	1.56	1.61	1.64	1.66
44	1.33	1.39	1.44	1.49	1.53	1.57	1.60	1.62
46	1.32	1.37	1.42	1.46	1.50	1.53	1.56	1.58
48	1.31	1.35	1.39	1.43	1.47	1.50	1.52	1.54

Determination of Paraffins and Naphthenes by Aniline Points

The determination of naphthenes in straight-run fractions is based on the same idea as that of aromatics. Straight-run fractions after the removal of aromatics (or cracked fractions after the removal of both aromatics and unsaturates) consist of naphthenes and paraffins. The percentage of naphthenes can be calculated on the basis of aniline points of the naphtheno-paraffinic fractions, provided the aniline coefficients for naphthenes (*i.e.*, the per cent by weight required to bring about the 1°C depression of the aniline point of paraffinic fractions) are known. This problem, however, is much more difficult than for aromatic hydrocarbons, since the depression of aniline points of paraffins by naphthenes is much less than that of paraffino-naphthenic fractions by aromatics; in other words, the aniline points of paraffins and naphthenes differ to a much smaller degree than do those of paraffino-naphthenic fractions and aromatics.

Fig. 18 represents the aniline points of paraffins (normal and branched) and monocyclic naphthenes (cyclopentanes and cyclohexanes),

boiling from 28 to 180°C, versus the boiling points. Three important conclusions can be made on the basis of Fig. 18:

(1) The curve for paraffins embraces both normal and branched paraffins. The higher or lower values of aniline points for isoparaffins, as compared with normal hydrocarbons, do not substantially change the picture for paraffins.

(2) The curve for naphthenes embraces both cyclopentanes and cyclohexanes.

(3) The difference between the aniline points of paraffins and naphthenes of the same boiling range decreases steadily with increasing boiling range of the hydrocarbons.

It should be pointed out that conclusions (2) and (3) are valid only for monocyclic naphthenes. Decalin (b.p. 190°C) for instance, has an aniline point of 33.6°C, *i.e.*, much below the curve for monocyclic naphthenes (about 59°C, according to the curve). This fact makes uncertain

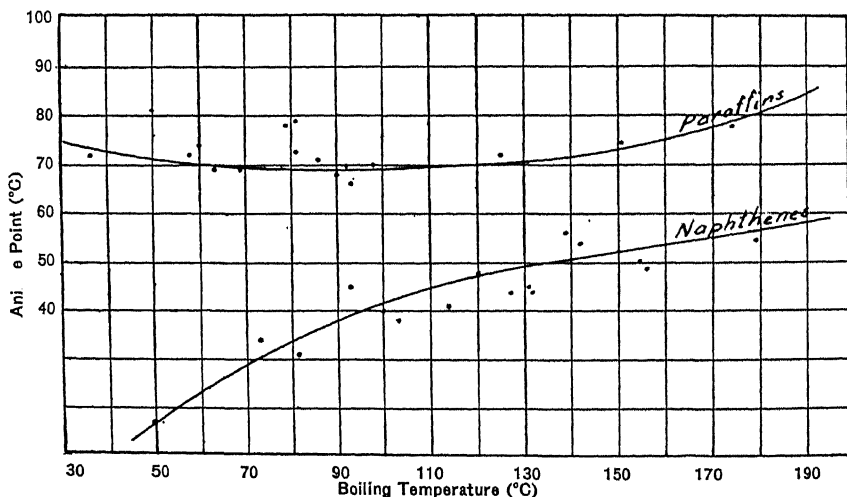


FIGURE 18. Aniline point of hydrocarbons versus boiling temperature.

and unreliable any determination of the content of naphthenes in fractions boiling close to 200°C, in which the presence of bicyclic naphthenes is probable, on the basis of aniline points.

For low-boiling paraffinic and naphthenic fractions up to 200°C (provided the naphthenic fraction, 150°-200°C, contains only monocyclic naphthenes) the curve of Fig. 18 gives the average data of aniline points shown in Table 31.

It should be remembered that the maximum aniline points and aniline points have practically the same values for paraffinic and naphthenic fractions.

Assuming a linear relationship between the aniline points and the composition of a paraffin-naphthenic mixture, calculation of the per-

Table 31. Average Aniline Points of Paraffinic and Naphthenic Fractions.

Boiling Range (°C)	Average Aniline Point (°C)		Difference (°C)
	Paraffinic Fraction	Naphthenic Fraction	
40-60	72	20	52
60-95	71	35	36
95-122	71	43	28
122-150	73	49	24
150-200	76	56	20

centage of naphthenes in paraffin-naphthenic fractions becomes a simple operation. Table 32 contains data for determining the content of naphthenes on the basis of aniline points of aromatic-free fractions containing only paraffins and naphthenes. The data for fractions from 150° to

Table 32. Determination of the Content of Naphthene Hydrocarbons by the Aniline Point Method.

Aniline Point (°C)	60-95°C Fraction	Content in Naphthenes by Weight		150-200°C Fraction
		95-122°C Fraction	122-150°C Fraction	
		Per Cent		
76				0
75				5
74				10
73				15
72			0	20
71			4	25
70	0	0	9	30
69	3	4	13	35
68	6	8	18	40
67	9	12	22	45
66	12	16	26	50
65	15	19	31	55
64	18	23	35	60
63	21	27	40	65
62	24	31	44	70
61	27	34	48	75
60	30	38	52	80
59	33	42	56	85
58	36	45	60	90
57	39	49	65	95
56	42	53	69	100
55	44	56	73	
54	47	60	77	
53	50	63	81	
52	52	67	85	
51	55	70	88	
50	58	74	92	
49	61	77	96	
48	64	81	100	
47	67	84		
46	70	87		
45	73	90		
44	75	93		
43	77	97		
42	80	100		
41	82			
40	85			
39	87			
38	90			
37	92			
36	95			
35	98			
	100			

200°C are valid only under the above assumption, namely, that bicyclic naphthenes are absent from the fraction, which seems to be the case for most straight-run gasolines.

As stated above, calculation of the content of paraffins and naphthenes on the basis of aniline points gives less accurate figures than that of aromatics. The average deviation of the calculated from the actual figures may be as high as 20 per cent.

For aromatic-free fractions boiling above 200°C the estimation of the content of naphthenes on the basis on aniline points seems impossible due to the presence of polycyclic naphthenes. Carpenter²¹ found that a 5 per cent addition of naphthenic hydrocarbons (pure naphthenic fractions produced from a crude) decreases the aniline point of aromatic-free kerosene fractions by 1°C. Thus he calculates the content of naphthenes in kerosene fractions by multiplying by 5 the difference between the aniline point of pure paraffins, boiling in the boiling range of a certain kerosene fraction, and the aniline point of the same fraction after the removal of aromatics. Since the aniline coefficient was determined only for a specific kerosene and for specific naphthenic fractions, it is obvious that the application of the coefficient in question must be limited to certain individual crudes.

Thus, the aniline method for determining the chemical composition of straight-run fractions involves the determination of two aniline points, before and after treatment with sulfuric acid. On the basis of these figures, the content of aromatics can be calculated for all fractions and that of aromatics, naphthenes and paraffins for fractions boiling below 200°C.

The method gives only the total percentage of aromatics present in a fraction, but in some cases the aniline points of hydrocarbon mixtures can be used for calculating the percentage of individual hydrocarbons. For instance, determination of aromatics in the fractions boiling between 60 and 95°C and between 95 and 22°C gives the percentage of benzene and toluene respectively, because of the virtual absence of any other aromatics in these fractions. Another interesting example is the analysis of the fraction containing normal butane and isobutane by the method of aniline or, better, orthotoluidine points (Francis^{41a}). There is a considerable difference in the orthotoluidine points of normal butane (32°C) and isobutane (12°C), and the percentage of such a mixture can be easily calculated with sufficient accuracy. Miller^{84a} applied the method of solvent points to determination of isomers in a heptane fraction.

Composition of Cracked Gasolines and Aniline Points

The method of aniline points for determining the chemical composition, described above in detail, relates to straight-run fractions and products which do not contain unsaturates. If a fraction contains unsaturates, the treatment with sulfuric acid removes aromatics and unsaturates, at least under certain conditions discussed in Chapter 3. Thus

the difference in aniline points before and after the treatment is caused by the aromatics and unsaturates, and the calculation of the content of both hydrocarbons is difficult because of the lack of data on the aniline coefficients of various unsaturates.

Garner⁴⁸ calculates the percentage of aromatics and unsaturates in cracked gasolines on the assumption that the unsaturates lower the aniline point approximately $\frac{2}{3}$ as much as the same percentage of aromatic hydrocarbons. Tilicheyev and Massine¹¹⁷ determined the aniline coefficients for olefins by preparing synthetic mixtures from pure unsaturated hydrocarbons separated from appropriate cracking fractions. Table 33 contains the aniline coefficients of the gasoline fractions for unsaturates and for aromatics. Maximum aniline points were determined in this case.

Table 33. Aniline Coefficients for Unsaturates and Aromatics.

Fraction (°C)	Aniline Coefficients for	
	Unsaturates	Aromatics
65-95	2.3	1.1
95-122	2.4	1.2
122-150	2.8	1.2
150-200	2.7	1.5

According to Tilicheyev and Massine, unsaturates lower the aniline point on the average $\frac{1}{2}$ as much as do aromatics; this is not too far from the figure of Garner, taking into consideration particularly the difference in the methods: that of aniline points was used by Garner and of maximum aniline points by Tilicheyev and Massine.

In addition to the aniline points before and after the removal of unsaturates and aromatics, the total amount of aromatics and unsaturates is determined by one of the conventional methods discussed in Chapter 3. The percentage of unsaturates is calculated by the formula:

$$Y = \frac{K_2(S - DK_1)}{K_2 - K_1},$$

where

Y = amount of unsaturates in per cent by weight;

S = total amount of aromatics and unsaturates in per cent by weight;

D = increase in the aniline point after the removal of aromatics and unsaturates;

K_1 = aniline coefficient for the aromatics;

K_2 = aniline coefficient for the unsaturates.

The figures for the content of aromatics and unsaturates obtained by these methods are very approximate because of insufficient data on the aniline coefficients for unsaturates.

The aniline point of cracked gasolines after the complete removal of aromatics and unsaturates can be used for calculation of naphthenes and paraffins in the same manner as in the case of straight-run gasolines (Table 32).

Determination of Aromatics by Specific Gravity and Refractive Index

As previously stated, the specific gravity and refractive index of narrow, straight-run fractions can also be used for determining the percentage of aromatics, naphthenes and paraffins. As with the method of aniline points, the determination of aromatics by specific gravity or refractive index gives the most reliable results because of the great difference in these properties for aromatics and for aromatic-free fractions of the same boiling range. A direct calculation of the percentage of aromatic hydrocarbons from the specific gravity (or refractive index) of a fraction before and after removal of aromatics and from the specific gravity of pure aromatics present in the fraction may give fairly reliable results. The calculation is made under the assumption that the specific gravity (or refractive index) of a hydrocarbon mixture is a linear function of the composition. Thus, the percentage of aromatics by volume is

$$X = \frac{100(D_1 - D_2)}{D - D_2},$$

where D , D_1 , and D_2 represent the specific gravity of pure aromatics, of the fraction before the removal of aromatics, and of the fraction after such removal, respectively.

However, mixing aromatic hydrocarbons with naphthenes and paraffins results in some expansion which involves a small error in the above calculation. Dunstan³² gives the following corrections due to the expansion, which must be added to the percentage found by the above formula:

% of Benzene or Toluene Calculated	Correction to Be Added	
	To Benzene	To Toluene
5	0.3	0.2
10	0.6	0.4
15	0.8	0.6
20	1.0	0.7
25	1.2	0.9
30	1.3	1.0

The percentage of aromatics by weight is calculated by the formula:

$$Y = \frac{100D(D_1 - D_2)}{D_1(D - D_2)}$$

Tilicheyev and Dumskaya¹¹⁶ determined the specific-gravity and refractive-index factors, *i.e.*, the increase in the specific gravity (or refractive index) effected by one per cent of aromatics, for various fractions boiling in the ranges 60-95°, 95-122°, 122-150° and 150-200°C. This method eliminates the use of corrections due to the expansion of mixtures. Thus, the percentage of aromatic hydrocarbons (by weight) in a fraction, Y , is calculated on the basis of the difference in the specific gravity (or refractive index) of the fraction before and after the removal of aromatics ($D_1 - D_2$) and of the factor C , according to the equation:

$$Y = \frac{D_1 - D_2}{C}$$

The factors in question are almost independent of the concentration of aromatics, if the concentration does not exceed 20-25 per cent. Table 34 contains data on the specific gravity and refractive index of mixtures of toluene with an aromatic-free naphtha fraction (boiling range 95-122°C).

Table 34. Factors of Specific Gravity and Refractive Index for Toluene.

Concentration	sp. gr. at 15°C	Factor of sp. gr.	Refractive index at 19°C	Factor of refractive index
0	0.7571		1.4167	
10.05	0.7656	0.00085	1.4230	0.00063
15.21	0.7705	0.00088	1.4265	0.00065
19.96	0.7746	0.00088	1.4295	0.00064

On the other hand, the factors depend upon the nature of the fraction boiling in the same range (Table 35).

Table 35. Factors of Specific Gravity and Refractive Index for Toluene.

Fraction	Conc of Toluene	Sp. gr. at 15°C	Factor of sp. gr.	Refractive index	Factor of refractive index
Paraffin-base	0	0.7327		1.4088*	
"	10.1	0.7437	0.00110	1.4158*	0.00069
Naphthenic base	0	0.7571		1.4185†	
"	10.05	0.7656	0.00085	1.4249†	0.00064
Methylcyclohexane	0	0.7729		1.4248‡	
"	10.33	0.7810	0.00078	1.4304‡	0.00057

*At 16.7°C. †At 20°C. ‡At 17.4°C.

Thus the factors for the same aromatic are lower for pure naphthenes and naphthenic fractions and higher for paraffinic fractions. The nature of aromatics also affects the factors for the same fraction (Table 36).

Table 36. Factors of Specific Gravity and Refractive Index for Various Aromatics Dissolved in a Paraffin-base Fraction (Boiling Range 130°-140°C).

Aromatic	Concentration (% by weight)	Sp. gr. 15°C	Factor of sp. gr.	Refractive index, 24°C	Factor of refractive index
Ethylbenzene	0	0.7464		1.4131	
"	20.02	0.7680	0.00108	1.4266	0.00068
<i>o</i> -Xylene	0	0.7470		1.4131	
"	20.03	0.7697	0.00114	1.4282	0.00075
<i>p</i> -Xylene	0	0.7470		1.4131	
"	20.14	0.7668	0.00098	1.4268	0.00068
<i>m</i> -Xylene	0	0.7468		1.4131	
"	20.15	0.7680	0.00105	1.4268	0.00068

Thus the specific gravity and refractive index factors depend upon the origin of fractions of the same boiling range, as well as upon the nature of aromatics, to a much greater extent than do the aniline point coefficients (compare Tables 26, 29, 35, 36). This affects considerably the reliability of the figures obtained by the methods in question. Some average factors must be used for each fraction.

Sachanen and Virobianz¹⁰⁷ found experimentally the specific-gravity and refractive-index factors for high-boiling 50°C fractions above 200°C

(atm. pressure). The aromatics which were dissolved in corresponding fractions have been mentioned in the previous section. Table 37 gives the average specific-gravity and refractive-index factors for various fractions on the basis of Tilicheyev-Dumskaya and Sachanen-Virobianz data. The factors vary for the same fraction, decreasing with increasing naphthenicity of the aromatic-free fractions.

Table 37. Factors of Specific Gravity and Refractive Index for Various Fractions.

Temperature range (°C) m. pressure	Sp. gr. of aromatic-free fraction	Factor of sp. gr.	Refractive index of aromatic-free fraction	Factor of refractive index
60-95	0.650 to 0.670	0.0016	1.39-1.40	0.0008
" "	0.670-0.700	0.0014	1.40-1.42	0.0007
" "	0.700-0.720	0.0013		
95-122	0.710-0.730	0.0011	1.40-1.41	0.0007
" "	0.730-0.750	0.0010	1.41-1.42	0.00065
" "	0.750-0.780	0.0009	1.42-1.43	0.0006
122-150	0.720-0.750	0.0010	1.41-1.42	0.0007
" "	0.750-0.770	0.0009	1.42-1.43	0.0006
" "	0.770-0.790	0.0008		
150-200	0.750-0.770	0.00095	1.42-1.44	0.0006
" "	0.770-0.795	0.0008		
200-250	0.780-0.810	0.0011	1.43-1.45	0.0008
" "	0.810-0.830	0.0009	1.45-1.46	0.0007
250-300	0.800-0.840	0.0012	1.44-1.45	0.0009
" "	0.840-0.870	0.0010	1.45-1.46	0.0008
" "			1.46-1.47	0.0007
" "			1.47-1.48	0.0006
300-350	0.810-0.820	0.0014	1.45-1.47	0.0009
" "	0.820-0.840	0.0012	1.47-1.49	0.0008
" "	0.840-0.870	0.0010		
350-400	0.820-0.830	0.0014	1.45-1.46	0.0010
" "	0.830-0.850	0.0012	1.46-1.47	0.0009
" "	0.850-0.880	0.0010	1.47-1.49	0.0008
400-450	0.830-0.850	0.0014	1.46-1.47	0.0010
" "	0.850-0.870	0.0011	1.47-1.48	0.0009
" "	0.870-0.900	0.0010	1.48-1.50	0.0008
450-500	0.840-0.865	0.0014	1.47-1.48	0.0010
" "	0.865-0.890	0.0011	1.48-1.49	0.0009
" "	0.890-0.910	0.0010	1.49-1.50	0.0008
500-550	0.865-0.880	0.0013	1.47-1.48	0.0010
" "	0.880-0.900	0.0011	1.48-1.49	0.00095
" "	0.900-0.910	0.0010	1.49-1.51	0.0008
" "	0.910-0.930	0.0009		

Table 37 shows that the factors increase considerably from the 150-200°C fraction to the 200-250° and 250-300°C fractions and then remain approximately constant. This jump in the factors is due to the polycyclic aromatic hydrocarbons which appear first in the 200-250°C fraction and which have a greater specific gravity and refractive index as compared with corresponding monocyclic aromatics.

The procedure of determining the percentage of aromatic hydrocarbons in a straight-run fraction by the above method is the same as for the method of aniline points. The fraction is appropriately treated with sulfuric acid for complete removal of aromatics. The specific gravities or refractive indices are determined before and after this treatment.

The percentage of aromatics is equal to the difference in the specific gravities or refractive indices before and after the treatment, divided by the corresponding factor of Table 37. The deviations of the figures calculated from the actual percentage may be as high as 10 per cent for low-boiling and 20 per cent for high-boiling fractions (above 200°C).

Table 37a presents data on the aromatic content of various fractions of a Baku crude oil. These data are calculated by the three methods—*aniline point*, *specific gravity* and *refractive index*—from the figures given by Sachanen and Virobianz.¹⁰⁷ The comparison of these data shows a satisfactory agreement between the three methods, the average deviation being of the order of 10 per cent with reference to the aromatic.

Table 37a. Content of Aromatics in Fractions of Baku Crude Oil, Determined by Different Methods.

Fraction, Boiling Range, (°C) at <i>n</i> pressure	% Aromatics by Weight Determined by		
	Aniline Point	Specific Gravity	Refractive Index
95-122	1	1	1
122-150	6	6	6
150-200	12	15	12
200-250	15	15	14
250-300	19	18	20
300-350	21	21	18
350-400	22	24	18
400-450	24	26	25
450-500	24	23	20
500-550	22	23	20

Determination of Paraffins and Naphthenes by Specific Gravity and Refractive Index

The determination of paraffins and naphthenes in aromatic-free fractions by specific gravity or refractive index of the fractions gives less reliable results. Figures 19 and 20 represent specific gravity and refractive index versus the boiling point of hydrocarbons, *i.e.*, paraffins and naphthenes (monocyclic cyclopentanes and cyclohexanes). The figures show clearly that the effect of the structure of paraffins (degree of branching) and naphthenes (number of carbon atoms in a ring, etc.) upon the specific gravity or refractive index at the same boiling range is much more pronounced than upon the aniline points. For this reason, the method of aniline points gives more reliable results than calculation of the percentage on the basis of specific gravities or refractive indices of the aromatic-free fractions. Francis^{42b} discussed the effect of structure on the properties of paraffins.

Table 38 gives the average values of specific gravity and refractive index of pure paraffinic and naphthenic fractions versus the boiling point on the basis of data summarized in Figs. 19 and 20.

The calculation of the percentage of paraffins and naphthenes in aromatic-free fractions can be made on the basis of the data of Table 38, assuming a linear relationship between the specific gravity or refractive index of the fraction and the composition.

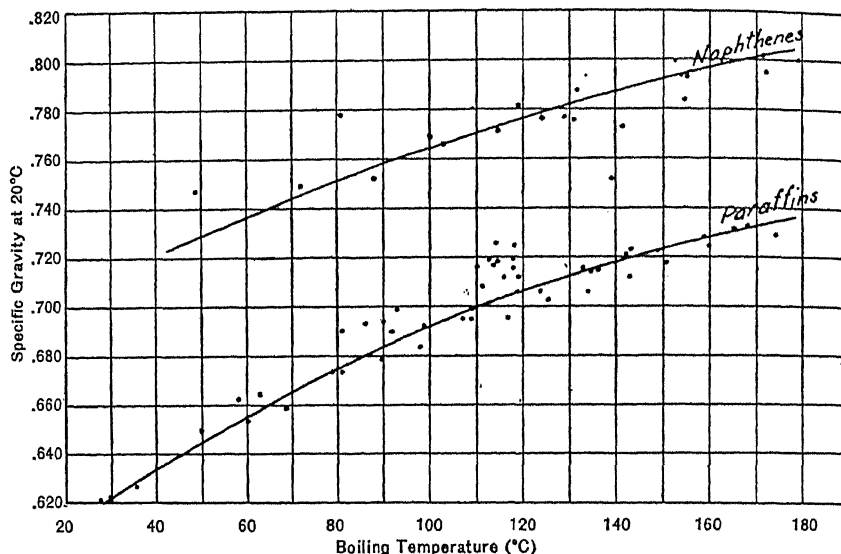


FIGURE 19. Specific gravity of hydrocarbons versus boiling temperature.

The equations on page 102 are used for this calculation, in which D , D_1 , and D_2 will represent specific gravity (or refractive index) of pure naphthenes, of the fraction to be tested, and of pure paraffins, respectively. It is understood that the boiling range of the pure naphthenes and paraffins should be the same as that of the fraction. The figures obtained should be considered as approximate, with a possible error up to 20 per cent (with reference to the percentage of naphthenes or paraffins).

No reasonable average data of specific gravity or refractive index can

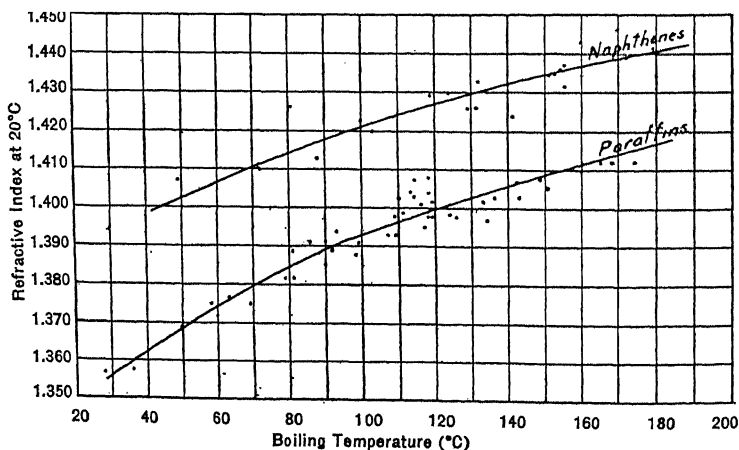


FIGURE 20. Refractive index of hydrocarbons versus boiling temperature.

Table 38. Average Values of Specific Gravity and Refractive Index of Pure Paraffinic and Naphthenic Fractions.

Boiling range (°C)	Specific gravity, 15°C		Refractive Index at 20°C	
	Paraffins	Naphthenes	Paraffins	Naphthenes
40-60	0.650	0.752	1.368	1.407
60-95	0.675	0.765	1.383	1.415
95-122	0.703	0.772	1.396	1.422
122-150	0.718	0.783	1.405	1.429
150-175	0.733	0.794	1.413	1.436
175-200	0.738	0.800	1.418	1.440

be assumed for high-boiling naphthenic fractions (above 200°C) because of the disturbing effect of polycyclization.

Refractivity Intercept Method

Kurtz and Ward⁶¹ showed that the refractivity intercept

$$\text{R.I.} = \text{Refr. Index} - \frac{\text{Density}}{2}$$

is nearly constant for hydrocarbons belonging to the same class. A summary of the data on the refractivity intercept for various hydrocarbons has been given by Ward and Kurtz.¹²⁸ The values of the refractivity intercept for the D-line are given in Table 39.

Table 39. Values of Refractivity Intercept.

Hydrocarbons	R.I.
Paraffins	1.0461
Naphthenes	1.0400
Aromatics	1.0627
Cyclic monoolefins	1.0461
Non-cyclic monoolefins	1.0521
Cyclic conjugated diolefins	1.0643
Non-cyclic conjugated diolefins	1.0877
Non-cyclic non-conjugated diolefins	1.0592

It should be noted, however, that aromatics or naphthenes with long paraffinic side chains have values of the refractivity intercept intermediate between those of paraffins and corresponding cyclic hydrocarbons. Thus the data of Table 39 relate to hydrocarbons of comparatively low molecular weight. The refractive intercept is approximately a linear function of the composition, like the specific gravity and other physical properties discussed above.

Kurtz and Headington⁶⁰ applied the refractivity intercept to the calculation of the composition of narrow cuts of gasolines. Conjugated diolefins are removed with maleic anhydride, as will be described in Chapter 3. Other olefins and aromatics are removed by sulfuric acid and redistillation (Chapter 3). The specific gravity and refractive index of aromatics plus olefins removed are calculated on the basis of the corresponding values of these properties before and after the treatment. The refractivity intercept of the aromatics plus olefins removed is then calculated. On the basis of this figure the percentage of aromatics, non-

cyclic and cyclic olefins is determined by graphical analysis. The amount of non-conjugated diolefins, cyclic and non-cyclic, is considered negligible. The refractivity intercept of the paraffinic and naphthenic fractions after separating olefins and aromatics, is used for calculation of paraffins and naphthenes.

The data on the method in question are insufficient to draw a final conclusion as to the reliability of this method. The individual deviations from the average figures of the refractivity intercept (Table 39) are in some cases very substantial (*e.g.*, Table 5 of the original article of Kurtz and Ward). For instance, the average difference between the refractivity intercepts for monoolefins and cyclic olefins is 0.0060, whereas the maximum and minimum deviations are from 0.0025 to 0.0029. In addition, the values of the refractivity intercept for paraffins and naphthenes, 1.0461 and 1.0400 respectively, are very close. Gooding, Adams, Rall and Smith^{44a} recently determined the refractive intercepts for narrow fractions of hydrocarbons in straight-run gasolines and thus improved the accuracy of the method.

Recently Donald³⁰ and Watson and Spinks¹³³ compared the results obtained for two Canadian straight-run gasolines by the method of aniline points and by the Kurtz-Headington method. In the first case the agreement was satisfactory, particularly for aromatic hydrocarbons, but in the second case it was very poor. It should be mentioned, however, that the two Canadian crudes of the same origin and very similar in properties, as well as in the properties of their fractions, gave widely different aniline points for the fractions treated with sulfuric acid. This

Table 40. Composition of Gasoline Fractions (Turner Valley Crude Oil)
Calculated by Various Methods.

Fraction No	Boiling Range (°C)	Method	—Composition (% by Weight)—		
			Paraffins	Naphthenes	Aromatics
4	100-125	Refractive intercept	43.0	46.2	10.8
		Aniline point	30.7	58.3	11.0
		Specific gravity	47	42	11
		Refractive index	35	54	11
5	125-150	Refractive intercept	57.9	17.5	24.5
		Aniline point	47.5	23.4	29.1
		Specific gravity	49	26	25
		Refractive index	49	24	27
6	150-175	Refractive intercept	52.1	22.2	25.7
		Aniline point	52.2	19.3	28.5
		Specific gravity	47	28	25
		Refractive index	51	23	26
7	175-200	Refractive intercept	38.0	42.9	19.1
		Aniline point	41.4	39.2	19.4
		Specific gravity			
		Refractive index	40	39	21

hardly is to be expected for two similar crudes. It is not improbable that the fractions of the second crude were overtreated with sulfuric acid and thus had an abnormally high paraffinicity after treatment.

In addition to Donald's data on the composition of the Turner Valley

gasoline fractions, calculated by the Kurtz-Headington and aniline-point methods, the composition of the same fractions was calculated by the author by the specific-gravity and refractive-index methods on the basis of the coefficients of Table 37 and of the data of Table 38. The calculations could be made only for fractions 4 to 7, since the boiling range of these fractions corresponds closely to those of Table 38. Calculation by the specific-gravity method for fraction 7 was impossible in view of the typographic error in the specific gravity of the dearomatized fraction. The data calculated by the four methods are summarized in Table 40. The agreement is satisfactory for aromatics, for which the maximum deviations of the figures produced by the four methods are in the neighborhood of 10-15 per cent. The deviations for the content of naphthenes and paraffins are greater.

Specific Dispersion

The specific dispersion is the difference in the refractive indexes for two specific wave lengths divided by the density measured at the same temperature as the refractive indexes.

Darmois²⁰ and Dixmier²⁰ were the first to show the fundamental difference in the specific dispersion between saturated and unsaturated hydrocarbons. Later investigations and data in this field were summarized by Ward and Fulweiler,¹²⁷ von Fuchs and Anderson⁴² and Grosse and Wackher.⁴⁰ These authors showed that at least a qualitative evaluation of the content of aromatic and unsaturated hydrocarbons on the basis of the specific dispersion is possible for any petroleum fraction, including high-boiling products.

The specific dispersion is usually determined for lines C (6563 Å) and F (4861 Å) or for C and g (4358 Å). For convenience, to avoid the use of fractions, the values of specific dispersion are multiplied by the factor 10,000. The temperature affects the specific dispersion to a very small extent, particularly in the narrow range of usual determinations from 15 to 30°C.

The specific dispersion of saturated hydrocarbons, aliphatic and cyclic, is practically constant and independent of the nature and molecular weight of hydrocarbons; it is 99 for the C and F lines and 155 for the C and g lines. The specific dispersion of unsaturates and aromatics is much greater, up to 200 for low-boiling aromatics and above 200 for conjugated diolefins (for the C and F lines). For high-boiling polycyclic aromatics the specific dispersion may be as high as 465. For the same class of unsaturated hydrocarbons, the specific dispersion changes with the boiling point, as Fig. 21 shows for hydrocarbons boiling in the range of gasolines (Grosse and Wackher).

Grosse and Wackher developed a method of determining the aromatic content of gasolines based on a specific dispersion of 99 for paraffins and naphthenes and the data for aromatics given in Table 41.

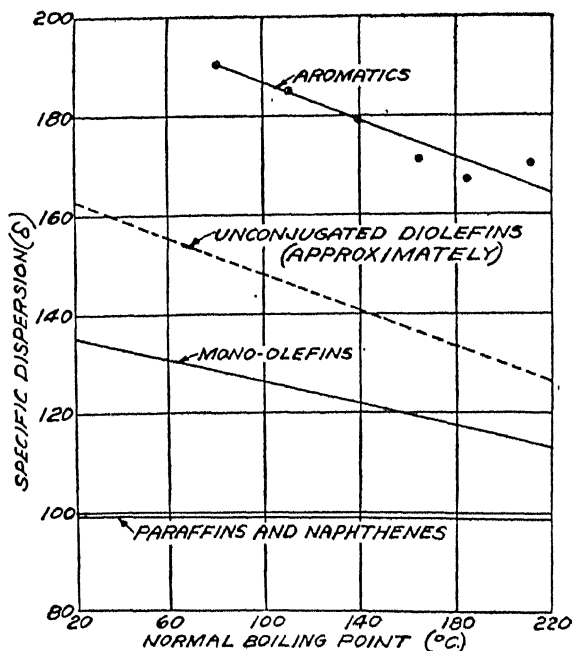


FIGURE 21. Specific dispersion versus boiling point for various hydrocarbon classes. (Courtesy Refiner and Natural Gasoline Manufacturer)

Table 41. Specific Dispersion of Aromatics.

Fraction (°C)	Aromatics	Specific Dispersion (Lines C and F)
70-95	Benzene	190.2
95-122	Toluene	184.9
122-150	Ethyl benzene and xylenes	179.2
150-175	C ₉ and C ₁₀ aromatics	175.0
175-200	C ₁₀ and C ₁₁ aromatics	171.0

The specific dispersion of a hydrocarbon mixture is additive and can be calculated by the mixture rule. Thus, the aromatic content of a straight-run fraction not containing unsaturates is calculated by the following formula:

$$x = \frac{\delta_{fr} - 99}{\delta_{ar} - 99} \times 100 \text{ per cent by weight,}$$

where δ_{fr} and δ_{ar} represent, respectively, the specific dispersion of the fraction and of the aromatics present in the fraction. The former is determined experimentally and the latter is given in Table 41.

In contrast to the methods of aniline points, specific gravity, etc., described above, it is not necessary to remove the aromatics from the frac-

tion. In fact the specific dispersion of the aromatic-free fraction will always be 99. The accuracy of this method is very satisfactory and better than that of the other methods discussed. However, it can be applied only to gasoline fractions, since the specific dispersions of high-boiling aromatics are as yet unknown. The extension of this method to high-boiling fractions is quite feasible, if the specific dispersions of high-boiling aromatics are determined.

The application of the specific refraction method to cracked gasolines containing unsaturates involves determination of the unsaturates. In this case the increase of the specific dispersion above 99 is due to the combined effect of aromatics and unsaturates. Grosse and Wackher estimate the effect of unsaturates in the following manner.

Conjugated diolefins produce abnormally high specific dispersions and, if present, should be eliminated by the reaction with maleic anhydride (Chapter 3). The relative amount of other unsaturates is estimated by bromine numbers determined by the Francis method. The authors found that the effect of the unsaturates can be calculated as follows:

$$\delta_{uns} = 99 + 0.16 \times \text{Br No}$$

Thus calculation of the percentage of aromatics in a cracked gasoline fraction is carried out by the formula:

$$x = \frac{\delta_{fr} - 0.16 \times \text{Br No} - 99}{\delta_{ar} - 99} \times 100$$

According to the authors, the maximum deviation is about ± 1.5 per cent aromatics. It should be borne in mind, however, that the authors used the same pure olefin in synthetic mixtures, which means that the determination of bromine numbers was performed under the simplest conditions. Much greater deviations should be expected for cracked gasolines containing various unsaturated hydrocarbons.

Viscosity Index and Viscosity-Gravity Constant

In addition to the specific gravity, refractive index and aniline point, various other physical properties or functions of oil fractions are related more or less closely to the chemical composition of the fractions. The viscosity index and viscosity-gravity constant are the best known of these.

The viscosity index is a function expressing the variation of viscosity of a product with temperature. As proposed by Dean and Davis,²⁸ this function is related to two reference lubricating oils, Coastal and Pennsylvania, which are characterized by a great and a small change of viscosity with temperature, respectively. The viscosity index of Coastal oils is accepted as zero, and that of Pennsylvania oils as 100. The viscosity index of any oil is calculated by the equation:

$$\text{V.I.} = \frac{L/V - U/V}{\frac{L/V - H/V}{L - U}} \times 100 \text{ or}$$

$$\text{V.I.} = \frac{L - U}{L - H} \times 100,$$

where U and V are the viscosities of the oil at 100 and 210°F, respectively (in Saybolt units), experimentally determined, L is the viscosity of a Coastal oil at 100°F, and H the viscosity of a Pennsylvania oil at 100°F, calculated from special tables, assuming that the Coastal and Pennsylvania oils have a viscosity at 210°F equal to that of the oil to be tested. The values of viscosity index may be between 0 and 100, as well as negative or above 100, indicating in the two last cases that they have a higher or lower temperature coefficient of viscosity than Coastal and Pennsylvania oils, respectively.

Another such function is the viscosity-gravity constant introduced by Hill and Coats.⁵² There is a close relationship between the viscosity and density of liquids. Batschinski⁷ found that for non-associated liquids the relationship is very simple, and is expressed by the equation:

$$\text{Viscosity} = \frac{c}{v - b},$$

where v is the specific volume of a liquid, and c and b are two constants. For associated liquids, particularly at low temperatures, the relationship between the viscosity and density is much more complicated. The viscosity changes with temperature much more rapidly than would be expected on the basis of the last equation. According to Hill and Coats, the relationship between the viscosity at 100°F in Saybolt units (V) and the specific gravity at 60°F (G) may be expressed as follows:

$$G = a + b \log (V + c),$$

where a , b and c are constants. The authors showed that the constant c is equal for all oils (38) and the constant b is a function of a :

$$b = \frac{1.0752 - a}{10}.$$

As a result, the viscosity-gravity constant, a , is expressed as follows:

$$a = \frac{10 G - 1.0752 \log (V - 38)}{10 - \log (V - 38)}.$$

Watson and Nelson¹³² introduced the so-called characterization factor K :

$$K = \frac{\sqrt[3]{T}}{S},$$

where T is the average boiling point of a fraction in °K and S the specific gravity at 60°F. K is approximately constant for various fractions of the same crude.

The values of viscosity index, viscosity-gravity constant and characterization factor for various distillates are summarized in Table 42.

Table 42. Viscosity Index, Viscosity-Gravity Constant and Characterization Factor of Various Products.

Product	Viscosity Index	Viscosity-Gravity Constant	Characterization Factor
1. Straight-run Pennsylvania lubricating distillates	100	0.800-0.805	12.2-12.5
2. Straight-run Mid-Continent lubricating distillates	80	0.830-0.840	11.8-12.0
3. Straight-run Coastal lubricating distillates	0	0.865-0.890	11.0-11.5
4. Solvent tars		0.88-0.95	10.0-11.0
5. Recycle stocks		0.90-0.95	10.0-11.0
6. Cracked residues		0.95-1.0	9.8-11.0

It should be pointed out, however, that the values of the above functions may give only a rough indication of the chemical composition of fractions or products. No calculation of the content of paraffins or paraffinic side chains, naphthenes and aromatics is possible on the basis of these functions.

It is of interest that all fractions of the same crude have approximately the same value for the function in question. Hill and Coats pointed out that the entire conception of the above functions "involves the assumption that the same general chemical composition, *i.e.*, the same degree of paraffinicity or naphthenicity, is characteristic of the successive fractions from any one individual crude." Tables 82 and 90 clearly show that this conception is surprisingly correct, at least for heavier fractions (gas oil and heavier) which have about the same percentage of paraffinic side chains, as well as of aromatic and naphthenic rings.

Correlation Index

The Bureau of Mines¹¹² developed the so-called correlation index for chemical characteristics of oil fractions. The correlation index has the same meaning as the viscosity index, but is based upon the specific gravity of the fractions, which depends upon their chemical character and boiling range. In order to eliminate the effect of the boiling range, the index correlates the specific gravity, G (at 60°/60°F), with the average boiling point of the fraction expressed in Kelvin degrees, K , in the following empirical formula:

$$\text{C.I.} = \frac{48,640}{K} + 473.7G - 456.8$$

The correlation index can be calculated for any fraction and thus is a more universal function than the viscosity index.

The values of C.I. are zero for normal paraffins and 100 for benzene. The naphthenes have intermediate values as, for instance, 51.4 for cyclohexane, whereas the C.I. of polycyclic aromatics is above 100 (*e.g.*, 124.9

for α -methylnaphthalene). The presence of paraffinic side chains decreases the index value.

The crude oils are fractionated by the standard Hempel method into 15 fractions and residuum. The boiling range of fractions, the average boiling points and equations for calculating C.I. are given in Table 42a.

Table 42a. Calculation of Correlation Index for Fractions.

Fraction	Pressure	Cut at °C	Average boiling point, (°C)	Average boiling point, (°K)	Equation for calculating C.I.
1	Atm	50			
2	"	75	58	331	$473.7G - 309.9$
3	"	100	82	355	$473.7G - 319.8$
4	"	125	107	380	$473.7G - 328.8$
5	"	150	131	409	$473.7G - 336.4$
6	"	175	155	428	$473.7G - 342.2$
7	"	200	180	453	$473.7G - 349.4$
8	"	225	205	478	$473.7G - 355.0$
9	"	250	231	504	$473.7G - 360.3$
10	"	275	257	530	$473.7G - 365.0$
11	40 mm	200	281*	554*	$473.7G - 369.0$
12	"	225	306*	579*	$473.7G - 372.8$
13	"	250	330*	603*	$473.7G - 376.1$
14	"	275	355*	628*	$473.7G - 379.3$
15	"	300	380*	653*	$473.7G - 382.3$

* Calculated temperature at atmospheric pressure.

C.I. values below 25 indicate the paraffinic nature of oil fractions, *i.e.*, the predominance of paraffins or paraffinic side chains. Values above 25 indicate increasing cyclization of hydrocarbons. They may be as high as 100 or higher, in which cases the crude oil has a highly polycyclic and aromatic character.

Application of the correlation index to the classification of crude oils will be discussed in Chapter 10.

Evaluation of Paraffin Isomers by Boiling Range and Parachor

There are no accepted methods for evaluating the extent of branching of paraffins present in petroleum fractions. In addition to the chemical methods described in Chapter 3, some physical methods may be of value in this respect.

The physical properties of various isomeric paraffins, such as specific gravity or refractive index, may vary to a considerable extent, but usually there is no direct relationship between the degree of branching and a given physical property. For instance, the specific gravity and refractive index of branched paraffins may be lower or higher, compared with those of the corresponding normal paraffin. Thus, these properties of a narrow paraffin fraction containing various isomers of the same molecular weight do not give any indication of the degree of branching.

Certain physical properties of isomers, however, change in one direction as compared with those of the normal paraffin. The boiling point of isomers, for instance, is invariably lower than that of the corresponding

normal paraffin; and in most cases, though not all, the greater the amount of branching the lower the boiling point.

Von Weber¹³⁴ calculates approximately the branching grade, Z , of a narrow paraffin fraction containing a normal paraffin and its isomers by the following equation:

$$Z = \frac{T_0 - T}{7},$$

where T_0 is the boiling temperature of the normal paraffin and T that of the fraction. It has been accepted that branching decreases the boiling point of the normal paraffin 7°C for each branch. The approximate evaluation of the branching can be carried out only for purely paraffin fractions, for instance, those produced from low-temperature alkylation products. By this method Von Weber determined that the extent of branching in various fractions of hydrogenated kogasin (synthetic gasoline produced by the Fischer-Tropsch method) is from 0.15 to 0.40. Thus, the paraffins in question consist mostly of normal and partially of mono-branched hydrocarbons. Calculation on the basis of the above equation may give only a very approximate idea of the degree of branching, since the boiling point decrement, accepted as 7°C for a single branching, actually varies from 4° to 9°C .

The molecular parachor is calculated by the equation:

$$\frac{\sqrt[3]{S}}{D - d} \times M,$$

where S is the surface tension, D and d the densities of the liquid and vapor respectively, and M the molecular weight. In most cases d is low as compared with D and may be omitted. This function was introduced by Sugden¹¹⁴ as similar to the molecular refraction. According to Sugden, the molecular parachor does not depend on the temperature, and can be calculated for hydrocarbons additively from the atomic parachor increments for C and H atoms and the ring increments. Mumford and Phillips,⁸⁵ however, found that chain branching affects the parachor, producing a negative increment (decrement) equal on the average to -3.0 for every branched group. They recalculated the values of atomic and structural parachors as follows:

CH ₂	40	Double bond	19
C	9.2	5-member ring	3
H	15.4	6-member ring	0.8
		Branching	-3.0

These data are sufficient to calculate the molecular parachor of all hydrocarbons which may be present in low-boiling oil fractions which do not contain polycyclic hydrocarbons. For instance, the calculated value of parachor for normal octane is 350.8 and the observed ones are 350.3

and 349.8. The negative increment for a single branch, -3 , exceeds considerably the experimental error from 0.5 to 1.0 in this particular case.

According to Waterman and Leendertse,¹³¹ the parachor data may give some evaluation of the degree of branching, although it would be premature to make any quantitative conclusions, for instance, by application of the increment -3 for a single branching.

Bauer⁸ found experimentally the following values of the molecular parachor for the three octanes:

<i>n</i> -octane	349.8
2-methylheptane	347.7
2,2,4-trimethylpentane	343.7

The value of the increment for a single branching is calculated to be only -2.0 from these experimental data.

Quayle *et al.*^{90a} found also that the effect of branching on the parachor is not uniform and varies to a greater extent than it was accepted earlier, depending upon the point of branching. The effect is increased as the branch is shifted toward the center of chain and as the length of the branch is increased.

Infrared and Ultraviolet Absorption; Raman Effect

The highly specialized techniques of infrared and ultraviolet spectroscopy, as well as of the Raman effect, are beyond the scope of this volume. The description of these methods can be found in the articles and books referred to in this section. Schlesman and Hochgesang^{110a} recently made a comprehensive survey of the methods in question, including the mass spectroscopy and x-ray method. It is also not the purpose of this section to give an exhaustive survey of experimental work on absorption spectra. Notwithstanding an enormous amount of investigation, application of these methods to elucidation of the chemical composition of petroleum so far is in the initial stage. It is hoped, however, that further development of the methods, particularly for very narrow fractions, may give far-reaching results.

The absorption of radiation by organic molecules is selective. As a result, only certain rather narrow ranges of waves are absorbed. The absorption bands depend upon the molecule itself, as well as upon certain groups and structures which are present in the molecule. Both infrared and ultraviolet radiations can be used to provide the absorption spectra, whereas hydrocarbons and most other constituents of petroleum are practically transparent to visible radiation.

The absorption bands of each hydrocarbon in a hydrocarbon mixture are almost independent of the other hydrocarbons. Thus, use of infrared or ultraviolet spectra permits qualitative and quantitative determination of certain structures or individual hydrocarbons present in a hydrocarbon mixture. The quantitative determination is based upon the intensity of the absorption bands characteristic of a given hydrocarbon structure.

Three units are used to measure the wave-length of absorption bands: microns (μ , or 0.001 mm), Angstrom units (\AA or 0.0001 μ), and reciprocal units or wave-numbers, ν , measuring the number of waves per cm:

$$\nu = \frac{10^8}{\lambda},$$

where λ is the wave-length expressed in Angstrom units. The wave-numbers which are directly proportional to frequency, are sometimes specified as frequencies.

The absorption of long-wave infrared radiation 7-25 μ , due mainly to changes in the vibrational energy of the molecule or its atomic framework, is highly individual, and may be different for isomers having very similar structures, such as *cis* and *trans* configurations. The shorter infrared absorption, 1 to 7 μ , is frequently related to vibrations of various structural fragments or radicals, such as CH_3 , CH_2 , etc. The ultraviolet absorption, due mainly to changes in electronic energy, is much less individual and depends upon the nature of the bonds between the carbon atoms, etc.; single, double and conjugated bonds between carbon atoms give different absorption spectra of short ultraviolet radiation, in the region from 2,000 to 4,000 \AA .

Infrared Absorption.*—Coblentz²⁴ found that petroleum fractions have fundamental absorption bands at 3.43, 6.86 and 13.8 μ , the two first ones of which correspond to H:C vibrations. These absorption bands have been found for paraffins, olefins and alkylated aromatic hydrocarbons.

Lecomte⁶⁸ reported on the infrared absorption spectra of various hydrocarbons in the region from 2.5 to 20 μ . With the exception of the fundamental H to C vibrations, the infrared absorption spectra in this region seem to be highly individual. As a result, those of various homologs, as, for instance, of paraffins or benzene derivatives, differ largely without any clear connection between the absorption bands and structural parts of the molecules. As will be seen later, some absorption bands in this region are characteristic of individual hydrocarbons.

Liddel and Kasper⁷⁰ and later Rose⁹⁶ made a comprehensive study of the infrared absorption bands from 1.8 to 1.1 μ (5,500 to 9,000 cm^{-1}) for various hydrocarbons. Most of the hydrocarbons were obtained from the National Bureau of Standards, where the hydrocarbons had been isolated from a Mid-Continent petroleum and carefully purified.

As mentioned above, the fundamental H to C vibrations absorbed by all hydrocarbons are not selective. They correspond to 2,900, 1,400 and 720 cm^{-1} (3.4, 6.8, and 13.8 μ). On the contrary, the absorption bands between 5,500 and 9,000 cm^{-1} (1.8 to 1.1 μ) reflect very closely the hydrocarbon structure. The absorption spectra of the paraffins have two dis-

* For further details and bibliography see "Infrared Spectroscopy," by R. Bowling Barnes, R. C. Gore, Urner Liddel and Van Zandt Williams, Reinhold Publishing Corp., New York, 1944.

tinct maxima corresponding to $8,300\text{ cm}^{-1}$ ($1.20\text{ }\mu$) and $8,400\text{ cm}^{-1}$ ($1.19\text{ }\mu$); two or three maxima in the region $7,000\text{--}7,900\text{ cm}^{-1}$ ($1.42\text{--}1.38\text{ }\mu$); and some maxima in the region $5,600\text{--}5,900\text{ cm}^{-1}$. The first two maxima are very specific and correspond to methylene ($8,250\text{ cm}^{-1}$) and methyl ($8,400\text{ cm}^{-1}$) groups. As a result the maximum, $8,250\text{ cm}^{-1}$, is relatively small for normal pentane and gradually increases with the molecular weight of normal paraffins. For such hydrocarbons as normal decane or dodecane, this maximum predominates. In contrast to this, the second maximum, $8,400\text{ cm}^{-1}$, corresponding to the methyl group, is strong for normal pentane and gradually decreases from normal pentane to normal dodecane. For the last hydrocarbon it is very slight. For highly branched isomers containing a large number of methyl groups, the absorption band $8,400\text{ cm}^{-1}$ is predominant. Figs. 22-25 illustrate the above generalizations.

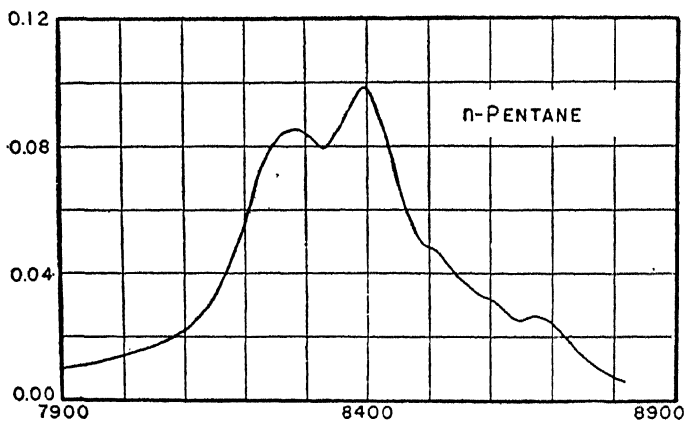


FIGURE 22. Specific absorption index versus wave number.

The absorption spectra of naphthenes in general correspond to the scheme given above. That of benzene is entirely different. It has no absorption bands corresponding to methylene and methyl groups, as might be expected. Benzene has a specific absorption band corresponding to $8,700\text{--}8,800\text{ cm}^{-1}$ ($1.14\text{ }\mu$) and representing aromatic C to H vibrations. The absorption bands in the range $7,000\text{--}7,200\text{ cm}^{-1}$ are insignificant. There are two sharp maxima between $5,900$ and $6,000\text{ cm}^{-1}$.

The absorption spectra of benzene homologs reflect the aromatic structure of the ring and the aliphatic structure of the paraffinic side chains. In addition to the characteristic aromatic absorption ($8,700\text{--}8,800\text{ cm}^{-1}$), the absorption bands of the methyl group ($8,400\text{ cm}^{-1}$), as well as those from $7,000\text{--}7,200$ and $5,600\text{--}6,000\text{ cm}^{-1}$, appear in the spectra of benzene homologs.

Barchewitz³ studied the absorption bands of very short-wave infrared radiation of $6,000$ to $10,000\text{ Å}$ (0.6 to $1.0\text{ }\mu$). In this region there are also certain bands specific for the methyl and methylene groups ($7,400$, $9,100$,

7600 and 9100 Å, respectively), as well as bands characteristic of groups containing a double bond, such as CH= , $\text{CH}_2=$ and C=C .

The double bond of aliphatic hydrocarbons has a very characteristic absorption band in a region of longer waves, at 6.10μ or $1,650 \text{ cm}^{-1}$. The total percentage of olefins in cracked gasolines may be determined on the

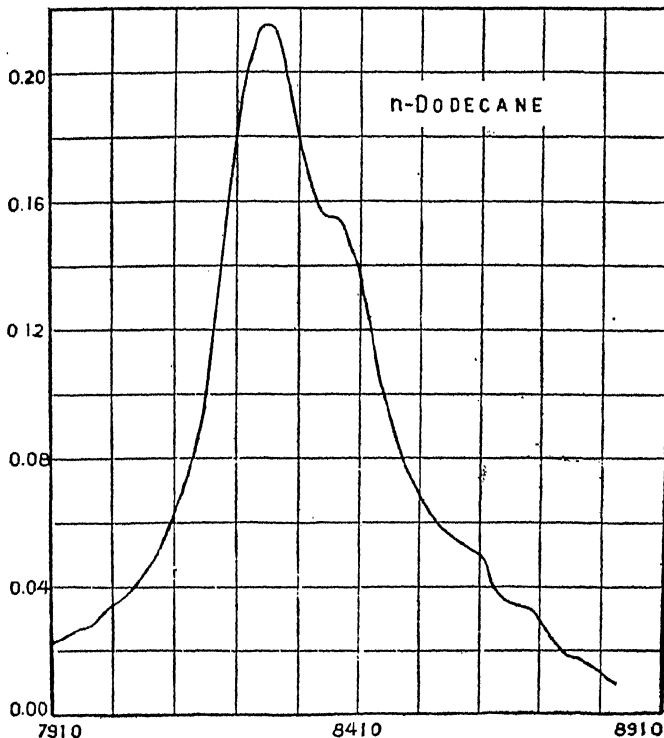


FIGURE 23. Specific adsorption index versus wave number. (Courtesy *Journal of Research of the National Bureau of Standards*)

basis of the intensity of this absorption band. In the same region of longer waves, the double bonds of benzene and its homologs give two characteristic absorption bands in the neighborhood of $1,600$ and $1,500 \text{ cm}^{-1}$. The last band is close to, but easily distinguishable from, one of fundamental bands corresponding to C-H vibrations.

It should be borne in mind that the position of the above absorption bands characteristic of various structures and given in terms of frequency or wave length is only approximate, and that it may shift if the general molecular structure changes. These shifts may be characteristic of certain structures. As shown above, the characteristic absorption band of aliphatic monoolefins (single double bond) corresponds to the frequency $1,650 \text{ cm}^{-1}$; for conjugated double bonds this band shifts to $1,600 \text{ cm}^{-1}$, and for the aliphatic double bond in styrene to $1,625 \text{ cm}^{-1}$.⁵

As a summary, the absorption bands in the region from 0.5 to 6.0 μ can be used for detecting and determining certain molecular structures. The individual hydrocarbons cannot be detected by this means. Some absorption bands corresponding to the wave length from 6 to 20 μ and related to vibrations of the whole framework may be characteristic of individual

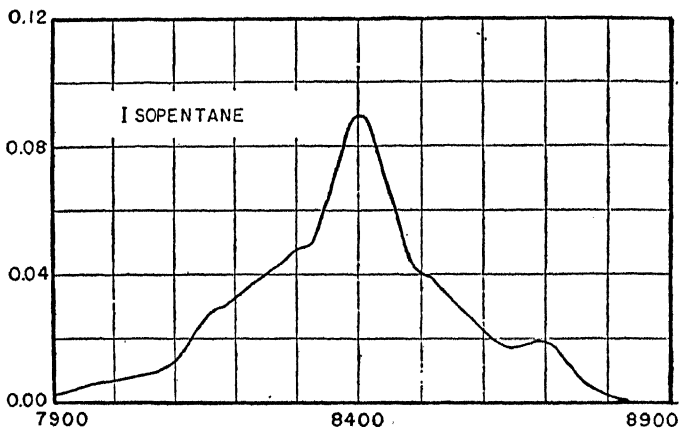


FIGURE 24. Specific absorption versus wave number.

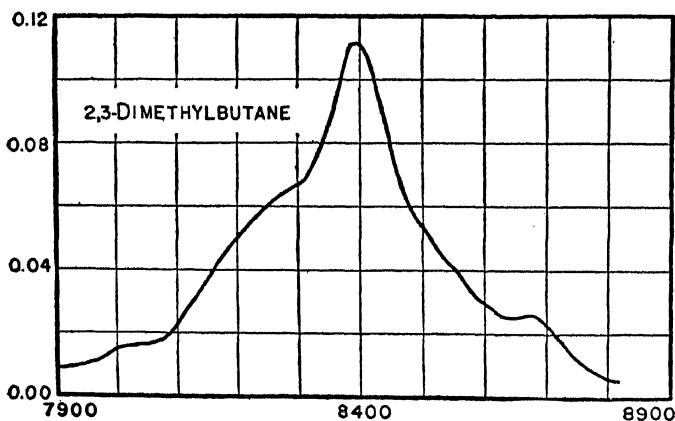


FIGURE 25. Specific adsorption versus wave number. (Courtesy *Journal of Research of the National Bureau of Standards*)

hydrocarbons, and may differ even for various isomers of the same hydrocarbon. These specific bands can be used for identification and quantitative determination of various hydrocarbons in a narrow fraction containing a limited number of individual hydrocarbons, not exceeding 6-8. The intensity of the absorption of the specific band of a given hydrocarbon is a quantitative measure of its concentration. By this method the percentage of hydrocarbons in C_4 -fractions may be determined with an accuracy

up to 1 per cent. For instance, in addition to the absorption bands corresponding to C-H and CH_3 structures, there are characteristic strong bands at 975-980 and 1,180-1,185 cm^{-1} for normal butane and isobutane, respectively. Quantitative determination of these hydrocarbons in the C_4 -fraction is based on the intensity of these bands. The presence of isopentane, however, would interfere with the determination, since this hydrocarbon also has an absorption band corresponding to 1,180-1,185 cm^{-1} . Thus the use of narrow fractions is a prerequisite for successful application of the method of infrared absorption. The analysis of the C_4 -fraction by the infrared absorption spectra has been recently discussed by Barnes, Liddel and Williams⁴ and Brattain.¹³

In addition to the analytical value of the infrared absorption, Rose⁹⁷ found that the method may be applied to determining the structure of unknown pure hydrocarbons. The molar absorption coefficient for a given wave-length, K , of paraffins dissolved in carbon tetrachloride is a linear function of their structure:

$$K = \alpha n_1 + \beta n_2 + \gamma n_3,$$

where α , β , γ are constants for all paraffins and for a given wave-length, and n_1 , n_2 and n_3 are the numbers of the methyl, methylene and CH groups, respectively. Thus, the determination of the molar absorption coefficient of an unknown paraffin for three wave-lengths would give three equations for determining n_1 , n_2 and n_3 , if the constants α , β and γ for the three wave-lengths are known.

Ultraviolet Absorption.—The ultraviolet absorption bands are characteristic of many structures. Benzene and its derivatives have bands in the region between 2,400 and 2,800 Å. The absorption bands of polycyclic aromatic hydrocarbons are displaced to the range of longer waves. For instance, naphthalene gives an absorption band in the region between 2,600 and 3,100 Å and phenanthrene in the region up to 3,700 Å.⁹⁷

Zerbe and Folkens¹⁴¹ measured the ultraviolet absorption for various fractions of a spindle oil. A comparative study of the ultraviolet absorption of naphthalene, anthracene, phenanthrene and chrysene was also carried out. These hydrocarbons show very specific curves for $\log K$ of the Lambert-Beer absorption equation ($J = J_0 \cdot 10^{-kcd}$, where J and J_0 represent the intensity of the initial light and that after absorption, c is the molar concentration and d the thickness of the substance) versus frequency in the range of 2,500 to 3,500 cm^{-1} . The lower fractions of spindle oil showed that the derivatives of naphthalene are predominant in these fractions. The higher fractions gave curves similar to that of phenanthrene.

Weizmann, Henri and Bergman¹⁸⁵ reported on the quantitative determination of aromatic hydrocarbons on the basis of ultraviolet absorption. The absorption bands of the following aromatic hydrocarbons were identified:

Benzene	2,433, 2,375 Å	Naphthalene	3,100 Å
Toluene	2,700	Phenanthrene	2,932
Xylenes	2,713, 2,739	Anthracene	3,500, 3,760

For the quantitative determination of these hydrocarbons, the intensity of the absorption bands for a given sample was compared with the intensity of the same bands for the standard substances in known concentrations. The fractions of an Iraq crude oil were investigated by this method, and the following concentrations of aromatics were determined:

Benzene	0.02 per cent	Naphthalene	0.30 per cent
Toluene	0.31 " "	Phenanthrene	1.36 " "
Xylenes	0.52 " "	Anthracene	1.76 " "

These investigators mention the limitations of this method applied to the determination of aromatics. Dialkylbenzenes with identical positions of the alkyl groups but substituted with different alkyls may give the same spectra. Alkylated polycyclic aromatics may give spectra identical with those of parent hydrocarbons.

The author believes that the presence of phenanthrene and anthracene in considerable proportions in a crude oil is not probable. Alkylated derivatives of partially hydrogenated phenanthrene and anthracene seem to be more likely constituents of crude oils.

Olefins have characteristic absorption bands in the region from 1,600 to 2,300 Å. A broad continuous band with its maximum near 1,750 Å is characteristic of most of the aliphatic olefins, as well as diffuse bands in the region from 1,900 to 2,300 Å.²²

Raman Spectra.*—The lines of the Raman spectra are caused by the scattering effect exerted by molecules illuminated with a source of exciting monochromatic light. As in the case of infrared and ultraviolet radiation, the Raman lines depend upon the molecular configuration, various structural parts of the molecule, and particular types of binding. The Raman frequency is the difference or the shift between the frequency of the exciting ray and that of the Raman ray, the frequency being expressed in terms of the reciprocals of the wave-lengths in centimeters. Thus the term "Raman frequency" used in the following paragraphs should be understood as the shift of the exciting frequency caused by the Raman effect.

Paraffin hydrocarbons have three main series of Raman lines. The first two series, between 2,800 and 3,000 cm^{-1} , and between 1,020 and 1,460 $^{-1}$, are effected by hydrogen-to-carbon oscillations, and the third one, between 300 and 350 cm^{-1} , by carbon-to-carbon oscillations. While the first lines do not depend on the isomeric structure of hydrocarbons, the frequency of the carbon-to-carbon lines is influenced by isomerization, as has been shown by Mecke,²³ who studied the Raman spectra of isomeric butanes, pentanes and hexanes. Strong absorption lines associated with the C-H bonds (2,880-3,000 cm^{-1} and in the region of 1,020 to 1,460 cm^{-1}) were identified for all hydrocarbons. The lines of lower frequencies vary

* See Hibben, J. H., "Raman Effect and its Chemical Applications," New York, Reinhold Pub. Corp., 1939.

from one isomer to another. Rosenbaum, Grosse and Jacobson¹⁰² studied the Raman spectra of isomeric hexanes and heptanes and arrived at the same results.

The double bonds have very sharp lines in the region from 1,600 to 1,680 cm^{-1} , which is free from the presence of other Raman lines.

The characteristic frequencies of the five- or six-carbon rings of cyclopentane and cyclohexane are in the range from 440 to 1,300 cm^{-1} . Benzene derivatives have the Raman frequencies of the double bonds and carbon-to-carbon bonds common with olefins and paraffins but, in addition to these, quite different frequencies characteristic of benzene.

The intensity of Raman lines is proportional to the concentration of a hydrocarbon. The mixture of various hydrocarbons will show all characteristic lines of individual hydrocarbons. As a result, at least in principle, the quantitative and qualitative analysis of simple hydrocarbon mixtures may be possible in some cases. It is understood that only colorless and non-fluorescing, "water-white" fractions can be used for analysis by Raman spectra. Colored or fluorescent petroleum fractions are treated with appropriate adsorbents to remove the substances causing these effects. It should be kept in mind, however, that this operation of treatment may remove, at least partially, not only objectionable substances but also certain hydrocarbons of the aromatic type.

The presence of unsaturated or aromatic hydrocarbons in petroleum fractions can be easily detected by Raman spectra because of the characteristic lines for double bonds and for aromatic structure.

Application of Raman spectra to wide fractions may give quite misleading results. For example, Andant² separated a Venezuelan spirit into a number of wide fractions and studied their Raman spectra. Benzene, toluene, ethylbenzene and mesitylene were determined as the main constituents of the fractions 60°-80°, 110°-127°, 133°-147° and 157°-176°C, respectively. It is highly improbable that there is a high concentration of aromatics in such wide fractions as these.

Grosse, Rosenbaum and Jacobson⁴⁸ applied the method of Raman spectra to the narrow paraffin fractions of alkylates produced by catalytic alkylation in the presence of aluminum chloride, boron fluoride and similar catalysts. The analysis was simplified by the absence of hydrocarbons other than paraffins. As has been stated above, the Raman spectra of isoparaffins give different lines in the region between 300 and 1,350 cm^{-1} . The Raman spectra of the narrow fractions in this region was compared to those of pure isomers. The presence and intensity of certain characteristic lines in the above region indicate the presence and quantity of isomers.

The olefins and aromatics present in narrow paraffin fractions can be eliminated by treatment with sulfuric acid or by sulfur dioxide extraction. The presence of about 10 per cent of naphthenes is not objectionable, as the intensity of their Raman spectra at such concentration is small. Rank, Scott and Fenske⁹¹ confirmed experimentally that the rela-

etc. The relative amount of ions corresponding to the different molecular weights constitutes an ionization pattern or mass spectrum. Such patterns differ not only for hydrocarbons of different molecular weight, but also for isomers; thus determination of various isomers is quite feasible by this method.

The mass spectroscopy method has so far been applied to hydrocarbons of molecular weight up to 238, but commercial application of the method has been limited mostly to the hydrocarbons including C_5 , as is the case with the Podbielniak analysis. Average errors are less than 1 per cent for most hydrocarbons and somewhat more for such hydrocarbons as butene-1 or butene-2. Hydrocarbons above C_5 also can be determined with a high degree of accuracy provided the mass spectra of the hydrocarbons are known. It is understood that the complex hydrocarbon mixtures must be separated into narrow fractions containing a limited number of individual hydrocarbons. Otherwise the mass spectra are too complicated for proper interpretations and calculations. The advantages of mass spectrometry are its rapidity and the use of very small samples.

X-ray Diagrams.—The application of x-rays to the study of petroleum has to date been limited mostly to solid constituents, such as petroleum waxes and asphaltenes. The x-ray diagram of solid paraffins and petroleum waxes enables one to determine the general structure of molecules as well as calculate the molecular dimensions and the distances between atoms. As might be expected, the normal paraffins show a zigzag chain structure. The distance between two carbon atoms, or the increment in spacing for CH_2 group, is 1.27 Å, and the increment for the hydrogen atom is 1.1 Å. Thus the two end-hydrogen atoms in the normal paraffin chain contribute 2.2 Å. The determination of the longitudinal molecular spacing, D , for pure normal paraffins by x-rays is sufficient for calculating the number of carbon atoms in the molecule, N :

$$N = \frac{D - 2.2}{1.27}$$

The x-ray diagram of isoparaffins shows a less symmetrical and less polar structure.

The x-ray diagram of asphaltenes was studied by Nellensteyn,^{8c} who found that the principal lines of the asphaltenes correspond to those of graphite.

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Chapter 3

Chemical Methods of Determining Hydrocarbons in Distillates

This chapter is confined to the chemical methods used to determine the chemical composition of petroleum distillates. It is assumed that the distillates to be studied by these methods consist entirely of hydrocarbons. As a matter of fact, the total oxygen, sulfur and nitrogen compounds present usually do not exceed from 0.1 to 0.5 per cent, particularly in low-boiling fractions. If the content of such compounds exceeds, say, 0.5 per cent, they must be removed by the methods described in Chapters 7 to 9. Otherwise, they may interfere with some hydrocarbons in various reactions described in this chapter. For instance, sulfuric acid used for separation of aromatics would also separate some sulfur compounds and most of the oxygen and nitrogen constituents.

Chemical methods may be classified as general methods, for determining the average structure of petroleum hydrocarbons, and as specific methods, for separating the specific classes of hydrocarbons, such as aromatics, olefins, diolefins, etc. The general methods are based upon the knowledge of the H:C ratio, or various other functions, before and after hydrogenation. The so-called ring analysis is closely related to these methods. The specific methods are purely chemical; they require specific reagents for separating various classes of hydrocarbons. Thus, sulfuric acid is employed for the separation of aromatics and/or unsaturates, bromine for the reaction with unsaturates, etc.

It should be pointed out that many very efficient reagents, which react strongly with hydrocarbons, cannot be used for determining the chemical composition of petroleum fractions, either because of their indiscriminate action on all classes of hydrocarbons or because they form too many reaction products which cannot be properly identified. For instance, aluminum chloride and chlorine attack practically all hydrocarbons and give a series of products for each hydrocarbon. Another example is formaldehyde which, in the presence of sulfuric acid, reacts with petroleum hydrocarbons, forming condensation products, the so-called formolites (Nastukov's reaction). A voluminous literature exists on the reaction between formaldehyde and hydrocarbons, but up to the present time there is no evidence that this reaction may be carried out specifically and completely for such hydrocarbons as unsaturates or aromatics.

In contrast to the physical methods described, the individual hydrocarbon, with few exceptions, cannot be separated by any chemical method.

Fractional distillation and crystallization are much more powerful methods for separating individual hydrocarbons than chemical methods, which, being less selective, usually separate the whole group of hydrocarbons reacting with the reagent used. A combination of the physical and chemical methods, however, gives the best results of separation, since the chemical methods, appropriately applied, simplify the final fractionation of individual hydrocarbons.

Most of the chemical methods relate to aromatic and unsaturated hydrocarbons which react readily with sulfuric or nitric acid, bromine, etc. Chemical methods are applied to the less reactive paraffins and naphthenes to a much less extent.

The chemical methods more or less widely used in petroleum chemistry at the present time may be classified as follows:

- (1) Determination of the H:C ratio.
- (2) Ring analysis.
- (3) Sulfonation of aromatic hydrocarbons.
- (4) Regeneration of aromatic hydrocarbons from sulfonic acids.
- (5) Nitration.
- (6) Reaction of aromatic hydrocarbons with picric acid.
- (7) Dehydrogenation of cyclohexanes into aromatic hydrocarbons.
- (8) Reactions of unsaturates with sulfuric acid.
- (9) Separation of unsaturated and aromatic hydrocarbons with sulfuric acid.
- (10) Separation of unsaturated and aromatic hydrocarbons with nitric acid.
- (11) Reaction of unsaturated hydrocarbons with sulfur monochloride.
- (12) Reaction of hydrocarbons with halogens.
- (13) Bromine and iodine numbers.
- (14) Separation of unsaturated hydrocarbons with mercurial salts.
- (15) Hydrogenation of unsaturated and aromatic hydrocarbons.
- (16) Separation of diolefins by condensation.
- (17) Reactions of tertiary hydrocarbons.
- (18) Oxidation of hydrocarbons.

Ultimate Analysis and H:C Ratio

The ultimate analysis of a narrow fraction in conjunction with the molecular weight gives the average empirical formula, on the basis of which the approximate structure of hydrocarbons composing the fraction can be estimated. The H:C ratio calculated from the empirical formula, as well as the percentage of hydrogen, will give the same results. The H:C ratio is usually expressed in terms of the number of hydrogen and carbon atoms, so that the H:C ratio for all monocyclic naphthenes and olefins is 2, independently of the molecular weight; for all other classes of hydrocarbons it changes with increasing molecular weight, decreasing for paraffins and increasing for the homologs of other classes.

It is accepted that petroleum fractions consist entirely of hydrocar-

bons, as has been mentioned above. If the content of non-hydrocarbon constituents exceeds 0.5-1.0 per cent, any conclusions on the basis of the H:C ratio or similar functions become misleading. The direct determination of the H:C ratio is made by the well known methods of the ultimate analysis of organic compounds, *i.e.*, by combustion methods.

A few words should be said, however, about various improvements in these methods, which were introduced mostly by the National Bureau of Standards and which made the determination of the H:C ratio very accurate. For instance, experimental determination of the ratio in moles $H_2O:CO_2$ for nonacosane gave 1.0343, 1.0345, and 1.0342, the theoretical ratio being 1.0345. Thus, the maximum deviation of the ratio experimentally found from the theoretical does not exceed 0.03 per cent.^{83, 153a}

The following improvements are responsible for the accuracy of the ultimate analysis:

(1) Oxygen used for combustion is completely freed from carbon dioxide, water, hydrogen and organic impurities.

(2) A quartz combustion tube contains platinized quartz and copper oxide.

(3) Hydrogen is used in the U-tube absorbers when weighing.

(4) Sealed connections are used in all connections, except for a ground-glass-to-quartz joint at the inlet end of the combustion tube, and ground-glass joints between the U-tube absorbers and the combustion tube.

The H:C ratio depends upon the ring structure, as well as upon the molecular weight of hydrocarbons of the same ring structure. The term "ring structure" means the number of rings in the molecule, the way they are combined, and their nature. At the same molecular weight, the H:C ratio is much lower for aromatic than for naphthenic rings. The same value of the H:C ratio may exist for a naphthenic hydrocarbon and for an appropriate mixture of an aromatic and a paraffin of about equal molecular weight. Thus, for simplification, petroleum fractions are completely and non-destructively hydrogenated so that the ring structure of the naphthenes formed corresponds to the original ring structure of the aromatics present in the virgin fraction. The H:C ratio is determined for the hydrogenated fraction.

Hydrogenation is carried out under high hydrogen pressure in the presence of nickel on kieselguhr at moderate temperatures to avoid decomposition, as will be described in a special section. The proof that hydrogenation is complete can be provided either by the specific dispersion, which equals 99 for pure naphthenes and paraffins (Chapter 2), or by the proper relationship between the specific refraction and aniline point. Fig. 27 represents the relation between the above properties for paraffin-naphthene mixtures of varying molecular weight, according to Vlугter, Waterman and van Westen.¹⁵² The aniline point of the completely hydrogenated product should agree with the value of the specific refraction read on Fig. 27.

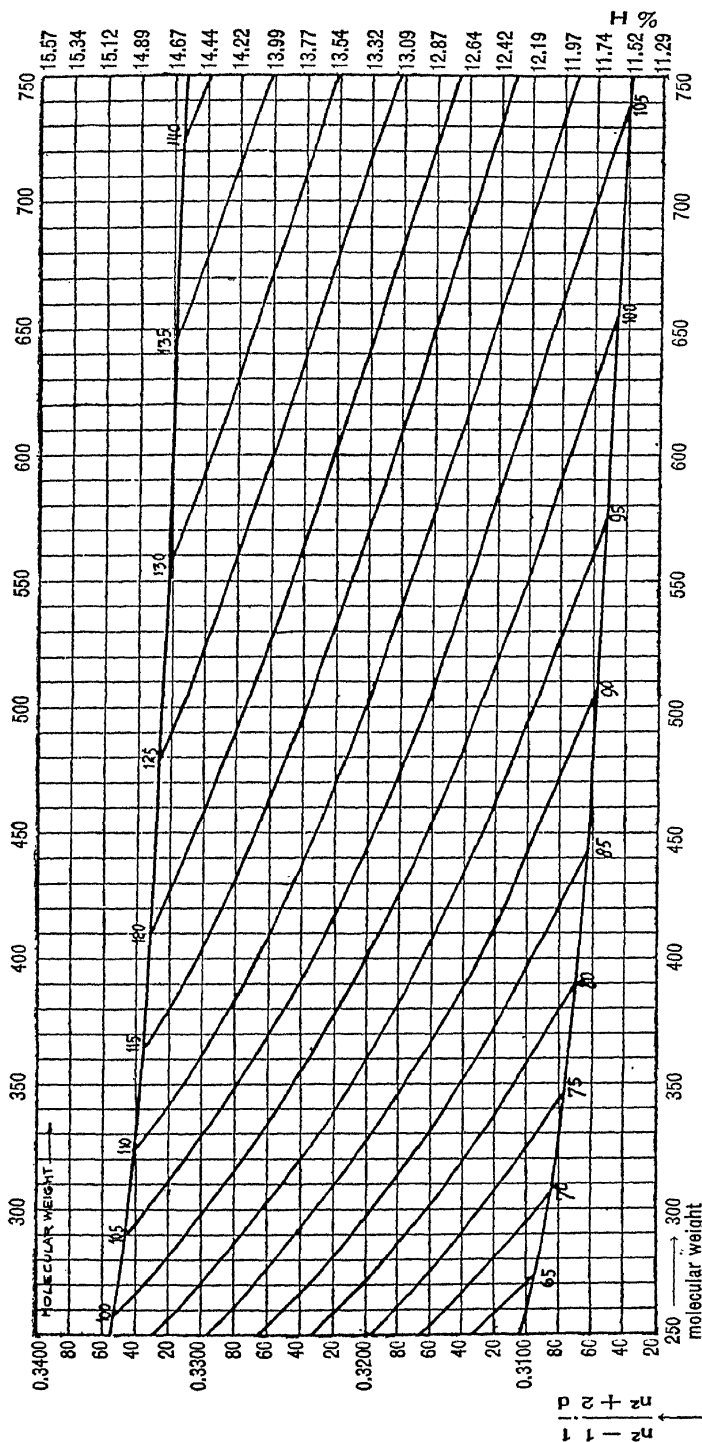


FIGURE 27. Relation between specific refractive index and aniline point for aromatic free oils. (Courtesy *Journal of the Institution of Petroleum Technologists*)

$$R = \frac{N^2 - 1}{N^2 + 2} \cdot \frac{1}{D}$$

where N is the refractive index for a certain wave and D the density at the same temperature at which the refractive index was determined. The specific refraction is independent of the temperature and is additive for many saturated hydrocarbons. Thus, the specific refraction of paraffins and five- and six-membered naphthenes can be calculated on the basis of the atomic refractions: it equals the sum of the atomic refractions divided by the molecular weight. Thus, a paraffin or naphthene of the formula C_nH_y has the specific refraction (for the sodium D Line):

$$R = \frac{2.418x + 1.100y}{12.01x + 1.008y} \text{ or}$$

$$\frac{y}{x} = \frac{12.01R - 2.418}{1.1 - 1.008R}$$

The atomic refractions in these equations are those of Eisenlohr.²⁸ The recent data of van der Hulst⁵⁶ for carbon (2.590) and for hydrogen (1.025) differ somewhat from the Eisenlohr data.

The close relationship between the H:C ratio and the specific refraction shows why both methods, *i.e.*, the direct determination of the ratio and the method of specific refraction, give practically the same results for paraffins and naphthenes.

Vlugter, Waterman and van Westen¹⁵² plot the values of specific refraction versus the molecular weight of hydrocarbons and obtain curves similar to those of Grosse. The application of these curves to narrow fractions gives the same results, but the experimental procedure is much simplified since the simple determination of refractive index replaces the elaborate ultimate analysis.

Fig. 29 represents the curves of the authors cited above. All monocyclic naphthenes (C_nH_{2n}) have the same specific refraction, 0.3294, which is independent of the molecular weight. In Fig. 29 the specific refraction of monocyclic naphthenes is a straight line (2) parallel to the X-line. The specific refraction of paraffins is curve 1 which is asymptotic to curve 2. The specific refraction of polycyclic naphthenes (C_nH_{2n-2} , C_nH_{2n-4} , etc.) are represented by curves 3 to 6, and that of condensed polycyclic naphthenes of the six-member type (without paraffinic side chains) is represented by curve 9. This curve starts with cyclohexane on curve 2, and continues through decahydronaphthalene on curve 3, etc.

As might be expected from the equation, given above, the curves of Figures 28 and 29 are quite similar. The percentage of hydrogen may be calculated from Fig. 29 on the basis of specific refraction.

The application and use of the Waterman's curves is very simple, but it should be kept in mind that the curves are based upon the preceding equations. Grosse pointed out that the presence of cyclobutane and cy-

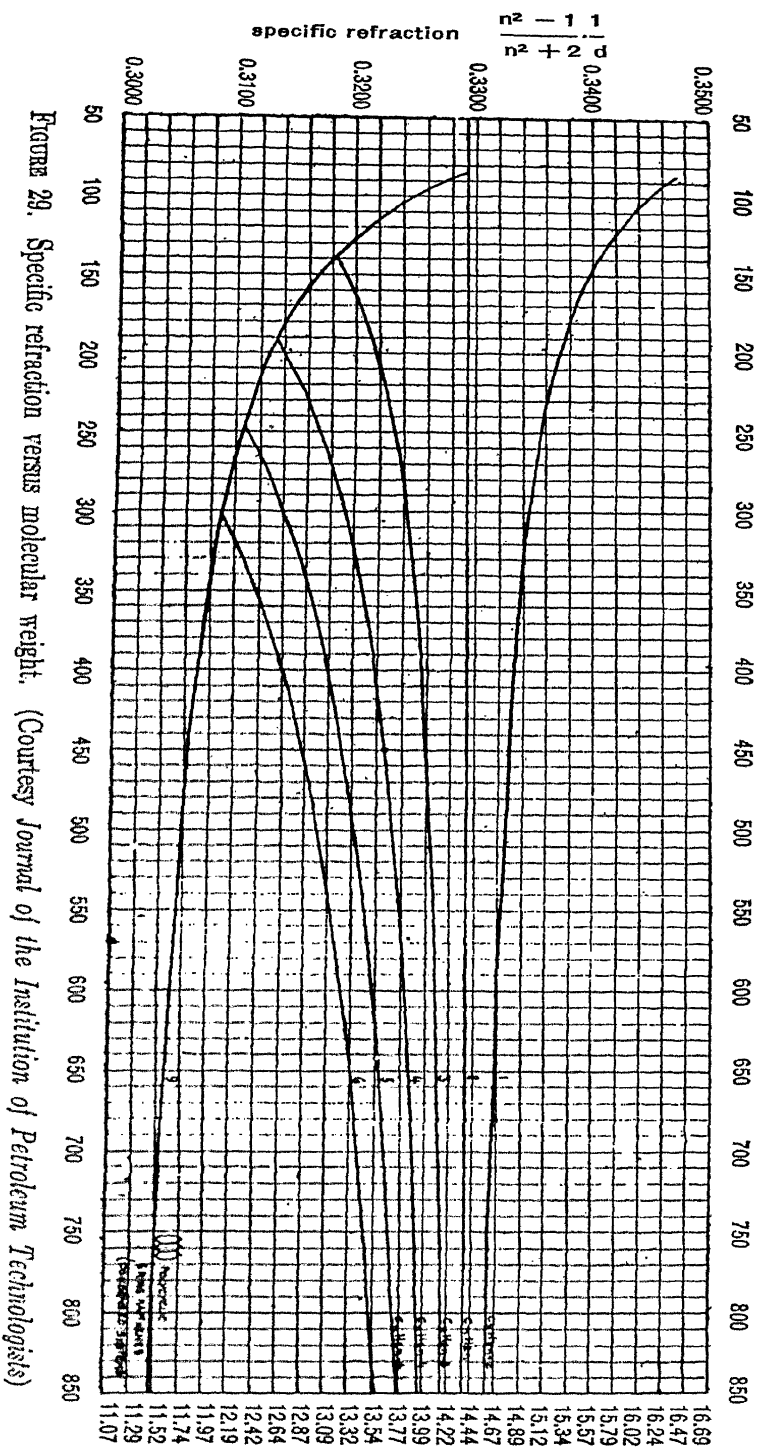


FIGURE 29. Specific refraction versus molecular weight. (Courtesy *Journal of the Institution of Petroleum Technologists*)

clopropane rings as well as of spirane carbons in polycyclic naphthenic structures cannot be excluded without experimental evidence. If such structures are present in petroleum fractions, the hydrocarbons will show optical exaltation or deviations from the equations. From this standpoint, direct determination of the H:C ratio may give more reliable results, which do not depend on the validity of the above equations.

The determination of the molecular weight of petroleum fractions may be carried out cryoscopically in naphthalene or benzene or ebullioscopically in benzene. The molecular weight of hydrocarbons or oil fractions usually increases with increasing concentration, because of deviations from ideal solution conditions at high concentrations. Thus, several determinations of the molecular weight are made at different concentrations, and the molecular weight is extrapolated to infinite dilution.

Other solvents, such as isooctane or normal heptane, can also be used for ebullioscopic determinations. Mair developed the technique of this method to such a degree that the accuracy of the determination of the molecular weight is ± 1 per cent.⁵¹

Ring Analysis

The chemical determination of various classes of hydrocarbons is based on certain reactions which occur specifically for each class. For instance, sulfonation of aromatics with concentrated sulfuric acid is considered a specific reaction for these hydrocarbons. Such hydrocarbons as cetylbenzene, however, are almost inert toward concentrated sulfuric acid because of the influence of a long paraffinic side chain which suppresses the aromatic properties of the hydrocarbon in question. This hydrocarbon appears to be paraffinic rather than aromatic. Another hydrocarbon, ethyltetrahydronaphthalene, also is neither a pure aromatic nor a pure naphthene, but a combination of an aromatic ring, a naphthenic ring, and a paraffinic side chain. Flugter, Waterman and van Westen¹⁵² proposed expressing the composition of such hydrocarbons, as well as of petroleum fractions, in terms of the percentage of aromatic rings, naphthenic rings, and paraffinic side chains. From this standpoint, cetylbenzene would consist of 25.5 per cent (by weight) aromatic rings (C_6H_5) and 74.5 per cent paraffinic side chains ($C_{16}H_{33}$). Ethyltetrahydronaphthalene would consist of 48 per cent aromatic rings (C_6H_4), 34 per cent naphthenic rings (C_4H_7) and 18 per cent paraffinic side chains (C_2H_5). Other authors express the percentage of rings and paraffinic side chains in terms of carbon atoms. Thus, ethyltetrahydronaphthalene would consist of 50 per cent aromatic rings (C_6), 33 per cent naphthenic rings (C_4) and 17 per cent paraffinic side chains (C_2).

According to the authors cited, the determination of the percentage of aromatic rings in straight-run fractions (not containing unsaturates) is carried out by hydrogenation. The aromatic-ring content may be easily calculated from the amount of hydrogen consumed. A pure aromatic without side chains, on hydrogenation, consumes on the average 7.8 per

cent of hydrogen (from 7.73 per cent for benzene to 7.92 per cent for anthracene). Thus, for instance, an actual consumption of 1 per cent of hydrogen would correspond to $\frac{1.0}{7.8} \times 100 = 12.8$ per cent of aromatic

rings in a petroleum fraction. However, determination of the actual hydrogen consumption is a very delicate and time-consuming operation, the results of which are difficult to reproduce. Instead of measuring the hydrogen consumption, the authors determine the aniline points of the fraction before and after hydrogenation. It has been experimentally found that the rise in the aniline point resulting from complete hydrogenation, multiplied by the factor 0.85, gives the percentage of aromatic rings (by weight). The coefficient 0.85 is valid for lubricating oils, but it changes for other fractions. For gas oils it is substantially greater, 0.93 according to Kreulen,⁷² and 1.00 according to Vlught, Waterman and van Westen.¹⁵³

The method of the non-destructive hydrogenation of petroleum fractions will be described in a special section, as well as the proofs of the completeness of the hydrogenation.

Fig. 27 may be used for an approximate estimation of the percentage of aromatic rings without actual hydrogenation, since the physical constants, including the aniline point, of the completely hydrogenated oils may be predicted from those of the original oils containing aromatic rings. For instance, an oil rich in aromatic rings has the following constants: molecular weight 362, aniline point 63.0°C, specific refraction 0.3239. According to Fig. 27, the aniline point corresponding to these values of molecular weight and specific refraction for a paraffinic-naphthenic oil is not 63.0°C but 100.9°C. The difference, 37.9°C, is evidently due to the presence of aromatic rings in the original oil. The authors found that this difference multiplied by the factor 0.80 equals the rise of the aniline point after complete hydrogenation.

After thorough hydrogenation the oil contains naphthenic rings and paraffinic side chains (and eventually "free" paraffins). The percentage of naphthenic rings and paraffinic side chains is determined on the basis of the molecular weight and specific refraction, or H:C ratio, of the oil. For instance, a completely hydrogenated oil has an average molecular weight of 450 and a specific refraction of 0.3225 (or 13.59 per cent of hydrogen). This oil is represented by a point in Fig. 29. As will be seen from the figure, this oil may be on the average either homogeneously tricyclic or a mixture of equal parts of dicyclic and tetracyclic naphthenes of an equal mean molecular weight, etc., or in an extreme case a mixture of paraffins and polycyclic naphthenes without paraffinic side chains (Curve 9, Fig 29). The interpolation between the curve of the paraffins (Curve 1) and the curve of the polynuclear naphthenes (Curve 9) gives the naphthenic ring content of the oil. The specific refraction of the par-

affins of molecular weight 450 is 0.3329, and that of the corresponding polycyclic naphthenes is 0.3063, thus giving the oil the following percentage of naphthenic rings:

$$\frac{0.3329 - 0.3225}{0.3329 - 0.3063} \times 100 = 39$$

plus 61 per cent of paraffinic side chains.

The following example illustrates the method of calculation. An original oil and a completely hydrogenated oil have the following properties:

	Original	Hydrogenated
Molecular weight	334	339
Refractive index n_D^{20}	1.5251	1.4858
Density d_4^{20}	0.9419	0.8932
Specific refraction	0.3254	0.3213
Aniline point ($^{\circ}\text{C}$)	62.0	94.0
Aniline point calculated from Fig. 27	—	93.8

The value of the molecular weight before and after hydrogenation is the same, which shows that no cracking occurred in hydrogenation. The value of the aniline point calculated from Fig. 27 is practically equal to the actual value, indicating that the hydrogenation of aromatics was complete. The aromatic ring content is

$$(94 - 62) \times 0.85 = 27 \text{ per cent by weight.}$$

The average molecular weight of a completely hydrogenated oil is 339 and the specific refraction 0.3213. The specific refractions of paraffins and condensed naphthenes of the same molecular weight are 0.3339 and 0.3078, respectively (Fig. 29). Thus the naphthenic ring content is

$$\frac{0.3339 - 0.3213}{0.3339 - 0.3078} \times 100 = 48 \text{ per cent by weight.}$$

Of these naphthenic rings 27 per cent were formed from aromatics by hydrogenation. Therefore the composition of the original oil is:

27	per cent aromatic rings,
21	" " naphthenic rings,
52	" " paraffinic side chains.

Calculation of the composition without actual hydrogenation is carried out as follows. From Fig. 27 the aniline point of the oil of molecular weight 334 and specific refraction 0.3254 is found to be 99.5°C . Thus the expected increase in the aniline point due to hydrogenation should be $(99.5 - 62) \times 0.8 = 30.0^{\circ}\text{C}$, and the percentage of aromatic rings $30 \times 0.85 = 25.5$ per cent. The aniline point of the hydrogenated oil should be $62.0^{\circ} + 30.0^{\circ} = 92.0^{\circ}\text{C}$. The specific refraction corresponding to molecular weight 334 and aniline point 92.0° is 0.3205, and the specific refraction of paraffins and polycyclic naphthenes of molecular weight 334

are 0.3337 and 0.3090, respectively. Thus the naphthenic ring content is calculated:

$$\frac{0.3339 - 0.3205}{0.3339 - 0.3090} \times 100 = 50 \text{ per cent by weight.}$$

Since the content of aromatic rings is 25.5 per cent, that of naphthenic rings in the original oil will be 24.5. Therefore the composition of the oil is:

25.5	per cent aromatic rings,
24.5	“ “ naphthenic rings,
50.0	“ “ paraffinic side chains.

The result is fairly close to the previous one obtained after actual hydrogenation of the oil.

As stated above, the use of ring analysis involves two basic assumptions: (1) that the naphthenes are of the six-ring type, and (2) that the polycyclic naphthenes are of the condensed type. Taking into consideration the presence of cyclopentanes in straight-run and cracked gasolines, as well as the structure of naphthenic acids, the occurrence of the five-ring structures in high-boiling fractions should be considered as not improbable. On the other hand, the polycyclic naphthenes, as well as the aromatics present in petroleum fractions are mostly of the condensed type, as will be seen later (Chapter 4). It should be pointed out, however, that the above figures for the percentage of paraffinic side chains and naphthenic rings would not deviate much, if, for instance, some polycyclic naphthenes were of the five-ring structure.

The backbone of the Waterman method—the calculation of the aromatic ring content by multiplication of the difference in the aniline point before and after hydrogenation by the factor 0.85—has been criticized and questioned by many authors. Neuman-Pilat and Pilat¹⁰³ found that the synthetic aromatic hydrocarbons dodecyl-*p*-cumene and α,β -dicarvacrylethane give very substantial deviations from the Waterman factor. According to Robinson,¹¹⁵ some individual aromatic hydrocarbons (diphenylhexane, diisooctyl-naphthalene) follow the Waterman factor and others (cyclohexyltetralin, heptylhydrinden) deviate in the same direction, as has been found by Neuman-Pilat and Pilat. Schicssler *et al.*¹²⁰ also found very substantial deviations for the following synthetic hydrocarbons: 13-phenylpentacosane, 5-phenyleicosane, 9-(2-phenylethyl)-heptadecane and 11-phenylheneicosane. The calculations for these hydrocarbons, the two of Neuman-Pilat and Pilat, and the two of Mikeska⁹² showed that the factor is 0.47 (instead of 0.85).

The above discrepancies between the behavior of the synthetic aromatics and aromatics present in lubricating oils may be explained thus. The factor in question depends upon the percentage of aromatic rings in the molecule. For highly aromatic hydrocarbons, such as xylenes, it is above 1.00. For the aromatics of kerosenes and gas oils, *i.e.*, with com-

paratively short paraffinic side chains, the Waterman factor is between 0.93 and 1.00, as has been stated above. The factor 0.85 corresponds to the aromatic hydrocarbons present in lubricating oils, which have somewhat longer side chains. Finally, the factor 0.47 has been found for synthetic monocyclic aromatic hydrocarbons which have paraffinic side chains exceeding 10 carbon atoms. As will be seen later, there are other indications that the aromatics of lubricating oils are polycyclic and have comparatively short side chains. Therefore, it is not thought necessary

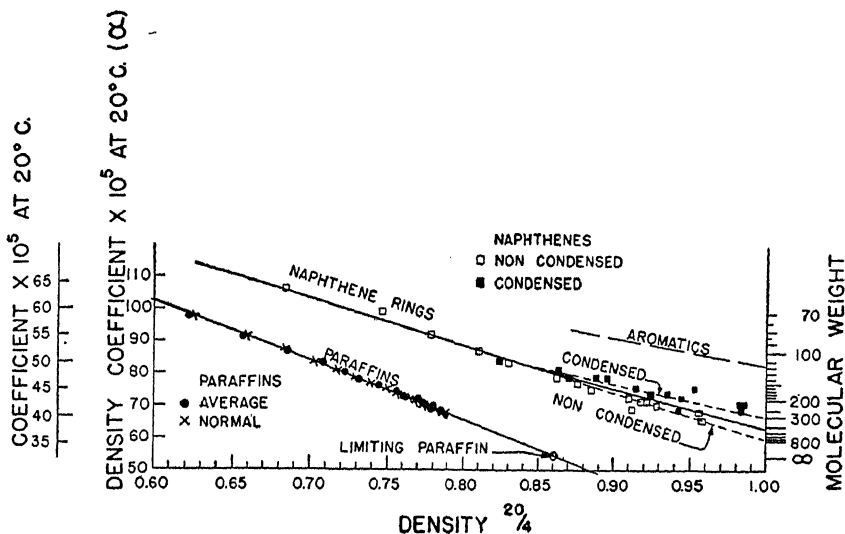


FIGURE 30. Density coefficient versus density. (Courtesy *Industrial and Engineering Chemistry*)

that the approximate value of the factor 0.85, obtained on the basis of experimentation with actual lubricating oils, should be drastically revised. Brancker^{11a} confirmed recently that the factor is close to 0.85 for petroleum aromatics.

It is understood that, in addition to the Waterman's method (H:C ratio or specific refraction), some other properties can be used for evaluation or calculation of the percentage of naphthenic rings or paraffinic side chains. Davis and McAllister¹⁹ found earlier that the molecular volume or viscosity index plotted versus the molecular weight form different curves for various classes of hydrocarbons. The number of carbon atoms in naphthenic rings may be represented as follows:

$$N = 0.358 \times \text{Mol. W.} + 7.7 - 0.3 \times \text{Mol. V.},$$

where Mol.W. and Mol.V. are molecular weight and volume respectively. This method can be used for calculation of the percentage of naphthenic rings in any hydrogenated oil or in such lubricating oils as Pennsylvania oils, which do not contain a considerable proportion of aromatics. Schies-

sler *et al.*¹²⁰ introduced a correction chart for the Davis-McAllister method.

Lipkin and Kurtz^{74, 79} suggested to calculate the percentage of naphthenic rings on the basis of relations between the temperature density coefficient at 20°C and density or the molecular weight and density. Fig. 30 represents the plot of density coefficients versus density for paraffins, and naphthenes, non-condensed and condensed. It should be pointed out, however, that the experimental data on the density coefficients are scarce, and the density coefficient data for the curves of Fig. 30 were calculated from the relationship between the density coefficient and molecular weight.⁷⁸ The method of density coefficients is extremely simple, requiring only two density measurements at two temperatures in the vicinity of 20°C. The calculation is practically identical with that of the Waterman method.

Lipkin and Kurtz⁷⁹ calculated the percentage of rings for a series of individual naphthenes by the Waterman method as well as by their own, and found that the former method gives more deviation than the latter. The average deviation for the Waterman method was found to be 12 per cent as compared with 7 per cent by the density method.

Schiessler *et al.*¹²⁰ also calculated the percentage of naphthenic rings for many synthetic naphthenes by different methods, including those of Waterman, Davis-McAllister and Lipkin-Kurtz. The Waterman method has given greater deviations from the theoretical values than the Lipkin-Kurtz and McAllister methods, the last one corrected by the "correction chart."

It should be pointed out, however, that the maximum deviations between the Waterman method and theoretical values have been found for monocyclic and polycyclic non-condensed naphthenes. It is not probable that the naphthenes of such structures are present in high-boiling oil fractions to any considerable extent. The presence of condensed naphthenes, as well as of aromatics, seems to be more probable, as will be seen in Chapter 4. It is of interest that the bicyclic condensed naphthenes studied by Lipkin and Kurtz and Schiessler *et al.* give close agreement between the theoretical percentage of naphthenic rings and that calculated by the Waterman method. In some cases for such hydrocarbons the latter method gives less deviation from theoretical than others, including the Lipkin-Kurtz method.

Thus the question of the relative merits of various methods applied to the determination of naphthenic rings, especially of the Waterman method, which is largely used at present, is still open. It should be pointed out, however, that criticism of the Waterman method was directed mostly to its broad application to various synthetic naphthenes, and not to the naphthenes which are actually present in high-boiling petroleum fractions. It is believed that application of the Waterman method to petroleum oils gives values of the content of naphthenic rings which are not far wrong.

The future development of the Lipkin-Kurtz method (density coefficient versus density) seems to be very promising, and the application of this method to various petroleum fractions would be of practical importance.

Deansley and Carleton²¹ suggested a modification of the Waterman method eliminating the use of aniline points. The linear relationship between the composition and specific refraction of saturated hydrocarbons may be expressed by the following empirical equation:

$$r = 0.2084 + 0.008421y,$$

where y is the percentage of hydrogen in a hydrocarbon or hydrocarbon fraction. For oils containing aromatics (or unsaturates) the equation must be corrected by an additional member representing the increment of the refraction due to the double bonds. The authors express this increment in terms of the unsaturation in grams of hydrogen per 100 grams of sample, h . Accordingly, for oils containing aromatics or unsaturates:

$$r = 0.2084 + 0.008421y + k'h,$$

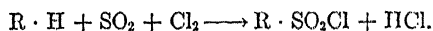
where k' is a constant depending upon the nature of aromatics (unsaturates). The relationship between this constant and the dispersivity $S - 98/h$ (S is the specific dispersion of the sample and 98 that of saturated hydrocarbons) is given in the form of an empirical equation and nomogram. The first step is the determination of h on the basis of the nomograms given. The determination of h permits calculation of the percentage of aromatic carbon atoms per molecule (in the absence of olefins and similar unsaturates). The total number of rings per molecule is calculated on the basis of the number of double bonds (in aromatic rings) per molecule and x in the general formula C_nH_{2n-x} of the sample. Other assumptions are the same as those made by Waterman.

The authors tried to extend the application of the method to petroleum oils containing olefins. The unsaturation due to the olefins is determined by the bromine-number method. Since the above methods do not give reliable figures for the olefin content in high-boiling fractions (see page 171), application of this method to such products seems doubtful.

At present it is impossible to evaluate the reliability of this method based largely upon the empirical relationship between the constant k' and the dispersivity. A comparison of results of the Waterman and "nomographic" analyses of various oils and blends made by the authors shows that the agreement between these methods is fair for oils which have a specific gravity below 0.95-96, and are not highly aromatic. For highly aromatic oils such as cracked oils, the agreement is poor, but it is questionable which of the two methods gives more reliable results. For instance, the value of 85 per cent of aromatic rings in an oil of specific gravity 1.0460 obtained by the Waterman method seems to be more reliable than the 46 per cent obtained by the "nomographic" method. An oil of such high specific gravity (M.W. 346) should be almost purely aromatic.

Sulfonation of Aromatics

The most general method of sulfonation of hydrocarbons has been recently developed by Reed,¹¹¹ and others.^{33, 146} Any hydrocarbon, aromatic, naphthenic or paraffinic, can be sulfonated by a gaseous mixture of sulfur dioxide and chlorine under the effect of actinic rays or certain catalysts:

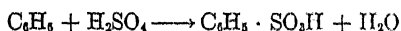


The sulfochloride formed is easily converted into a corresponding sulfonic acid by hydrolysis. The reaction was studied by Kharasch and Read,⁶⁵ Helberger,⁴⁷ and Schumacher and Stauff.¹³⁰

The general character of this method is apparently based upon the action of chlorine in the first stage of the reaction and of sulfur dioxide in the second stage. Any hydrocarbon is attacked by chlorine under proper conditions in contrast to sulfuric acid, which is much more selective in its sulfonating action. In view of the general character of the reaction, this method cannot be used for separation of different classes of hydrocarbons, at least in the present stage of development.

On the contrary, sulfuric acid is a reagent for aromatics and unsaturates, whereas paraffins and naphthenes do not react with it at low temperatures, at least when the concentration of the acid is below 100 per cent and the reaction time is not excessive.

Sulfonation of aromatics with sulfuric acid as, for instance,



produces sulfonic acids quantitatively or almost quantitatively. The reactions of sulfuric acid with unsaturated hydrocarbons are quite different and will be discussed in a special section. This section is confined to the reaction and separation of aromatics with sulfuric acid in the absence of unsaturates, *i.e.*, in straight-run products and fractions not containing olefins and other unsaturated hydrocarbons.

The formation of monosulfonic acids seems to be the only reaction which takes place between aromatic hydrocarbons and concentrated sulfuric acid. Polysulfonic acids are not formed; their formation takes place either at higher temperatures or with an excess of fuming sulfuric acid. The treatment of petroleum products or fractions with sulfuric acid in laboratory or commercial practice is carried out at low temperatures. Even in commercial treatment with fuming sulfuric acid, only monosulfonic acids are formed, since the fuming acid is employed in a comparatively small proportion and is thus diluted almost instantaneously with the water formed.

The structure of sulfonic acids corresponds to that of the original aromatic hydrocarbons. In some cases, however, the sulfonation of aromatics is complicated with isomerization and disproportionation reactions, particularly for polyalkylated aromatics. Jakobson⁵⁸ showed that sulfonation of 1,2,4,5-tetramethylbenzene causes partial isomeri-

zation into 1,2,3,4-tetramethylbenzene and formation of pseudocumene and hexamethylbenzene. Sulfonation of pentamethylbenzene gives 1,2,3,4-tetramethylbenzene and hexamethylbenzene; as the latter is not sulfonated, it forms an upper layer on sulfuric acid. Smith and his co-workers¹⁸⁴⁻¹⁸⁷ studied numerous rearrangements of this type for various polymethyl- and polyethyl-benzenes. It is not believed that these complications are very significant in the sulfonation of petroleum fractions, as these do not contain a large proportion of highly polyalkylated aromatics.

The aromatic hydrocarbons of all petroleum fractions form sulfonic acids which are soluble in water. On the contrary, the solubility of sulfonic acids in petroleum depends upon the molecular weight and structure of the acids. The sulfonic acids produced from low-boiling fractions are insoluble in petroleum because of the short paraffinic side chains of such acids. The sulfonic acids produced from high-boiling fractions may be soluble ("brown" or "mahogany" sulfonic acids) or insoluble ("green" sulfonic acids). Both "brown" and "green" sulfonic acids are monobasic, and the difference between them apparently is due mainly to the structure of paraffinic side chains. The "brown" sulfonic acids are derivatives of polycyclic aromatic hydrocarbons with comparatively long paraffinic side chains which are the cause of their solubility. The "green" acids are a result of the sulfonation of some highly polycyclic aromatics or aromatic resins with very short paraffinic side chains.

It should be pointed out that neither the "brown" nor the "green" sulfonic acids are uniform; they may consist of various sulfonic acids more or less soluble in petroleum. As the medium boiling-point fractions such as non-viscous lubricants are sulfonated, they form sulfonic acids which are soluble in hot oils and may precipitate on cooling.

If a petroleum product contains a large proportion of resinous and asphaltic materials, the acid sludge after sulfonation may contain, in addition to "green" acids some constituents which are insoluble in water. These compounds of unknown structure are formed from the asphaltic and resinous components.

The sulfonic acids formed from aromatic hydrocarbons with short paraffinic side chains are soluble in sulfuric acid and thus are completely removed in an acid sludge containing an excess of sulfuric acid. In such cases the volume loss of the original product after sulfonation equals the volume of aromatics sulfonated and removed with the sludge, provided that the absorption of hydrocarbons by the sludge is negligible (page 146).

The sulfonic acids formed by aromatic hydrocarbons with long paraffinic side chains are easily soluble in the unreacted oil, as has been mentioned above. The oil is separated from the sludge and then treated with alcohol-water to remove the dissolved sulfonic acids. In such cases, the difference between the original volume of the oil and the volume after sulfonation and extraction of sulfonic acids is a measure of the volume

of aromatics sulfonated. It should be pointed out, however, that the last procedure is not always feasible because emulsification takes place on extraction and causes considerable losses.

The concentration of sulfuric acid for sulfonation and for complete removal of aromatic hydrocarbons is a very important factor of the method discussed. Diluted sulfuric acid does not affect aromatic hydrocarbons. Fuming sulfuric acid is the strongest sulfonating agent, but its use is undesirable because of its oxidizing and dehydrogenating action. As a result, six-membered naphthenes are dehydrogenated with fuming sulfuric acid into aromatics which react with an excess of the reagent and produce sulfonic acids; excessive figures for aromatics may be obtained in this way. Isoparaffins also react with fuming sulfuric acid, producing various oxidation products.

The concentration of sulfuric acid used for quantitative and selective removal of aromatics should be rather moderate to avoid side reactions involving naphthenes and isoparaffins. This and other problems of the method used for determining aromatics are discussed below and separately for straight-run gasolines and heavier straight-run products, including gas oils and lubricating oils.

As the equation on p. 142 shows, the reaction of sulfonation is accompanied by formation of water, which is dissolved in the excess sulfuric acid used. As a result, the sulfuric acid is gradually diluted and loses its sulfonating capacity. For instance, the initial concentration of sulfuric acid of 98 per cent, taken in the volume ratio 1:1 for sulfonation of 20 per cent benzene solution in an aromatic-free gasoline, is reduced to 95.1 per cent after complete sulfonation. It will be reduced to only 97.1 per cent, if the volume ratio of sulfuric acid to gasoline is 3:1. In addition, sulfuric acid is diluted with the sulfonic acids formed, which are soluble in sulfuric acid and reduce its concentration. Thus sulfuric acid is employed for sulfonation in considerable excess to avoid dilution of the reagent as much as possible. Such high volume ratios of sulfuric acid to petroleum as 3:1 are customarily used, corresponding to an excess of acid of about 15 to 30 times with respect to the aromatics present.

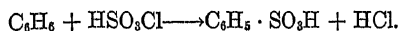
Kattwinkel⁶⁸ recommended adding phosphoric pentoxide to sulfuric acid to bind the water formed. In the Kattwinkel modification 30 gr of phosphoric anhydride are dissolved in 100 cc of concentrated sulfuric acid (98%).

The sulfonation of petroleum oils for separating aromatic hydrocarbons is carried out at room temperature, or at lower temperatures down to 0°C. As will be seen later, varied temperatures, for instance from 0 to 30°C, may be used for selective sulfonation of certain aromatic hydrocarbons. Any appreciable increase in temperature, particularly for high-boiling fractions, should be avoided to prevent oxidation and other side reactions. If unsaturates are absent, the reaction of sulfonation of aromatics is accompanied by a slight increase in temperature.

As will be seen later, the sulfonation of aromatic hydrocarbons is used mostly for purposes of separation. The identification of aromatic hydrocarbons by sulfonic acids can be employed in some cases. For this purpose the sulfonic acid produced is converted into sulfonyl chloride and then to the corresponding amide. Chambers and Watt¹⁶ use *s*-benzylthiuronium chloride for producing *s*-benzylthiuronium derivatives of sulfonic acids. They give the melting points of a series of such derivatives of many sulfonic acids formed from benzene and naphthalene hydrocarbons.

The direct methods of identifying sulfonic acids, however, may be used to a limited extent only, since the data on the properties of sulfonyl amides and other derivatives of aromatic sulfonic acids are scarce and insufficient.

Chlorosulfonic acid is sometimes used for sulfonation instead of sulfuric acid. Sulfonation by this reagent proceeds for benzene according to the following equation:



Volatile hydrogen chloride is formed instead of water in sulfonation with chlorosulfonic acid. As a result, dilution of the reagent is practically eliminated. Under proper conditions chlorosulfonic acid is a more powerful sulfonating agent than concentrated sulfuric acid. It should be kept in mind, however, that chlorosulfonic acid attacks isoparaffins slowly (page 186).

A modification of the conventional sulfonation method is the use of liquid sulfur dioxide as a solvent, which dissolves aromatic hydrocarbons and the sulfonating agent (sulfuric or chlorosulfonic acid). Grob and Adams³⁸ patented this process. Thus, the reaction between aromatic hydrocarbons and a sulfonating agent takes place in the same phase. Numerous patents were issued later along the same line. Ross *et al.*¹¹⁷ recently revised the use of liquid sulfur dioxide for this and other reactions. The procedure is as follows. The aromatic hydrocarbon to be sulfonated is mixed with liquid sulfur dioxide at low temperatures up to -15°C . Commercial oleum or chlorosulfonic acid is also dissolved in liquid sulfur dioxide at the same temperature and then mixed with the aromatic hydrocarbon dissolved in the same solvent. The time of the reaction is only a few minutes. When the reaction is complete, the mixture may be treated with ice water which dissolves the sulfonic acids formed. The sulfur dioxide is removed by evaporation. Sulfonation by this method proceeds under thoroughly controlled conditions and apparently gives better results than the conventional method. To the best knowledge of the author, this modification of the sulfonation method has not been applied to the separation of aromatic hydrocarbons in petroleum products.

Sulfonation of paraffins and naphthenes with sulfuric acid seems to be feasible under certain conditions, at least for some of these hydro-

carbons. Worstall¹⁰² sulfonated normal heptane and octane by fuming sulfuric acid on a steam bath with reflux condenser and produced sulfonic acids in yields claimed to be from 30 to 40 per cent. The greater part of the paraffins was oxidized to carbon dioxide and water. The conditions for sulfonation of paraffins differ greatly from those for aromatics; as a result, the separation of aromatics by the methods described does not affect paraffins and naphthenes to any extent.

Separation of Aromatics in Gasolines by Sulfonation

Tilicheyev and Dumskaya¹⁴² extensively investigated the sulfonation of low-boiling aromatics with sulfuric acid. They used solutions of numerous aromatics in varied concentrations in aromatic-free gasolines. The solutions were treated with sulfuric acid of several concentrations. Aromatics boiling in the range of gasolines, *i.e.*, benzene and its derivatives, including amylbenzenes, react readily with 94-100% sulfuric acid. Lower concentrations are insufficient to effect the complete removal of aromatics. Benzene is an aromatic hydrocarbon very resistant to sulfonation. By using 3 volumes of sulfuric acid per volume of gasoline and 30 minutes of shaking at room temperature, it was impossible to sulfonate benzene dissolved in gasoline completely, if the concentration of sulfuric acid was lower than 98-100 per cent. Under the same conditions, toluene, xylenes, ethylbenzene *etc.* were completely sulfonated by 94 per cent sulfuric acid. Thus a complete removal of aromatics from gasoline can be obtained by treatment with 3 volumes of 98-100 per cent sulfuric acid per volume of gasoline. The treatment is carried out in a shaker for 30 minutes. It should be mentioned that 98 per cent sulfuric acid can usually be used instead of 100 per cent. In fact, its use seems to be preferable because of the possibility of interaction between paraffins and naphthenes containing tertiary carbon atoms and 100 per cent acid. Fisher and Eisner³² found, for instance, that 100 per cent sulfuric acid, as well as the Kattwinkel reagent, readily attack branched paraffins and cyclohexane derivatives (1 volume of the hydrocarbon, 3 volumes of the acid reagent, shaking for 5 minutes at room temperature). The standard method of the Institution of Petroleum Technologists adopted the treatment with 2 volumes of 98 per cent sulfuric acid for 15 minutes and two subsequent treatments with one volume of fresh acid. The time necessary for a complete separation of gasoline treated and freed of aromatics is usually 6 hours.

As stated above, sulfonic acids produced from benzene derivatives of straight-run gasolines are soluble in the excess of sulfuric acid and thus are removed with the sludge. Therefore the volume of aromatics sulfonated equals the difference between the original volume of the gasoline and that after the treatment. In some cases such determinations give reliable results on the percentage of aromatics present in straight-run gasolines. In other cases, however, the percentage of aromatics calculated by the decrease in the volume of a gasoline after the

treatment is too high, because of absorption of paraffins and naphthenes by sulfuric acid.

Thus it is recommended that the percentage of aromatics be determined by an indirect method. The treated and aromatic-free gasoline is separated from the sludge, neutralized with dilute sodium hydroxide, washed with water until neutral, and dried with calcium chloride. Then a certain physical property of the aromatic-free gasoline is determined, such as specific gravity, refractive index, aniline point, etc., as well as the same property of the original gasoline. The calculation of the percentage of aromatics is carried out by the methods described in Chapter 2. The indirect methods usually give more reliable results than the direct method. The gasoline to be analyzed is separated into fractions corresponding to the main aromatic hydrocarbons, as described in Chapter 2. Each fraction is separately sulfonated and treated by the above procedure.

Separation of Aromatics in High-boiling Fractions by Sulfonation

The determination of aromatics by sulfonation in high-boiling fractions, from kerosene to lubricating oils, is a more difficult problem for two reasons. First, aromatics with long paraffinic side chains lose their aromatic properties to a certain degree and do not react easily with concentrated sulfuric acid. Secondly, the sulfonic acids formed from heavy oils are readily soluble in oils and insoluble in the sludge. As a result, the sulfonic acids are accumulated in the treated oil and must be removed by washing.

According to Tilicheyev and Dumskaya¹⁴² and Shreve and Lux,^{133a} the derivatives of naphthalene with short side chains, *i.e.*, methyl and dimethyl naphthalenes, are easily and completely sulfonated even by 93 per cent sulfuric acid. On the other hand, Tilicheyev and Kuruindin¹⁴³ found that the solubility of hexyl and heptyl benzenes in 98 per cent sulfuric acid is only partial, whereas such aromatics as undecyl or cetyl benzenes are completely insoluble and do not react with this reagent. Fuming sulfuric acid, however, even with a small excess of anhydride, *e.g.*, 101 per cent, completely sulfonated aromatics with long paraffinic side chains.

The results of Nametkin and Robinson¹⁰⁰ do not agree completely with those of Tilicheyev and Kuruindin. According to Nametkin and Robinson, such hydrocarbons as cetylbenzene, isocetylbenzene and isocetylnaphthalene, and their solutions in an aromatic-free fraction can be sulfonated with 98.2-100.6 per cent sulfuric acid.

It should be pointed out that the high-boiling petroleum fractions are sulfonated much more easily than might be expected on the basis of the investigations cited above. It is well known, for instance, that the aromatics of lubricating oils can be easily sulfonated even by 94 per cent sulfuric acid. Treatment of transformer, turbine and lubricating oils with 94 per cent sulfuric acid gives high yields of sulfonic acids even

in the absence of an excess of the reagent. This phenomenon may be attributed either to a particular structure of the aromatics of high-boiling fractions or to the comparatively short paraffinic side chains of petroleum aromatics. The latter suggestion seems to be particularly probable. The aromatic hydrocarbons have very low, strongly negative viscosity indices so that the removal of the aromatics invariably increases considerably the viscosity indices of the oils treated. According to Mikeska,⁸² the viscosity index of hexylnaphthalene is -66, whereas that of dihexyl naphthalene increases to 53. Thus it is probable that the number of carbon atoms in paraffinic side chains of aromatics does not exceed five or six.

Sachanen and Virobianz^{123, 124} extracted aromatic hydrocarbons from high-boiling fractions with sulfur dioxide and added the aromatics extracted to various aromatic-free, high-boiling fractions. The aniline points and specific gravities of the aromatic-free fractions were determined before and after the addition of the aromatics. Then the fractions with the aromatics were treated with 2-3½ volumes of 98 per cent sulfuric acid. The aniline points and specific gravities were determined after the treatment and compared with those of the original fractions (Table 43).

Table 43. Removal of Aromatics from High-boiling Fractions with Sulfuric Acid.

Boiling range at 1 atm (°C)	% aromatics added	Volume ratio H ₂ SO ₄ to oil fraction	Aniline point			Specific gravity		
			Original	arom. added	After treatment	Original	arom. added	After treatment
200-250	14.2	3½	78.9	70.1	78.7	.791	.806	.791
250-300	20.4	3½	77.8	66.0	78.0	.845	.869	.847
350-400	17.7	2	94.0	85.8	94.4	.825	.850	.825
400-450	29.0	2	97.8	83.6	98.8	.850	.888	.850
450-500	31.7	2	103.8	89.2	103.6	.871	.923	.872
500-550	19.2	2	106.0	97.8	106.2	.904	.930	.904

The data of Table 43 show that the sulfonation and removal of the aromatics added by 98 per cent sulfuric acid is complete.

In Table 44 there are some data on specific gravities and aniline points of certain high-boiling fractions after treatment with 2 volumes of 98 per cent sulfuric acid and after an additional treatment with 2 volumes of 101 per cent fuming sulfuric acid.

Table 44. Properties of Fractions after Treatment with Sulfuric Acid.

Boiling range at 1 atm (°C)	After treatment with 98 per cent H ₂ SO ₄		After treatment (1) with 98 per cent H ₂ SO ₄ and (2) with 101 per cent H ₂ SO ₄	
	D ₁₅	Anil. P., °C	D ₁₅	Anil. P., °C
400-450	0.869	95.4	0.863	97.2
450-500	0.885	102.6	0.881	103.6

Table 44 indicates that additional treatment with fuming acid does not change appreciably either the specific gravity or the aniline point of the fractions treated. Additional treatment with fuming sulfuric acid decreases the specific gravity or increases the aniline point to the

extent corresponding to 3 to 5 per cent of aromatic hydrocarbons which would not be extracted in the first treatment with 98 per cent sulfuric acid.

The results obtained by Robinson¹¹⁵ are close to those of Sachanen and Virobianz. For instance, he treated a lubricating fraction, $n_{20}^D = 1.4950$, with 98 per cent sulfuric acid and dearomatized the fraction to refractive index 1.4740, whereas with 100.5 per cent sulfuric acid the aromatic index fell to 1.4690. The approximate calculation of the aromatic content, according to Table 37, gives 28 per cent by the first method (98 per cent acid) and 32 per cent by the second modification (100.5 per cent acid), whereas Robinson's figures are 23 and 29.6 per cent, respectively. It is very likely, however, that the effect produced by fuming sulfuric acid is due, at least partially, not to the aromatics removed but to the polycyclic naphthenes dehydrogenated by the acid and then sulfonated. Thus, it appears that the treatment of high-boiling petroleum fractions with 2 to 3 volumes of 98 per cent sulfuric acid is sufficient to remove by far the greatest part of the aromatic hydrocarbons.

Nametkin and Robinson,¹⁰⁰ however, recommend aromatics from high-boiling fractions to treat them twice with 3 volumes of 100.6-100.8 per cent fuming sulfuric acid at 20°C for 30 minutes. They claim that paraffins and naphthenes are not affected under these conditions.

According to Rossini,¹¹⁸ lubricating oils contain aromatic rings in combination with naphthenic rings as, for instance, in tetrahydronaphthalene. Such "mixed" aromatics as tetrahydronaphthalene have very pronounced aromatic properties and react readily and completely with sulfuric acid of even moderate strength. The behavior of more naphthenic aromatics, as, for instance, containing three naphthenic rings and one aromatic ring, toward 94 and 98 per cent sulfuric acid is not known. It is very likely that 100 per cent acid will completely sulfonate such hydrocarbons.

The solubility of sulfonic acids with comparatively long paraffinic side chains in a treated oil is another complication. Nametkin and Robinson observed that some sulfonic acids with long side chains are insoluble either in the treated oil or in sulfuric acid and form a separate layer between the oil and the sludge (acid).

The separation of sulfonic acids which are dissolved in the oil treated or forming an intermediate layer is carried out as follows. The oil (and the intermediate layer, if present) is treated with water-alcohol mixture (1:1) and then allowed to separate for at least 24 hours. Sulfonic acids are readily soluble in water-alcohol and do not form strong emulsions. The oil free of sulfonic acids is neutralized with weak (1% Bé) water-alcohol sodium hydroxide solution, washed and dried. The extract of the sulfonic acids separated may be evaporated under moderate temperature conditions to remove the solvent (water-alcohol). The sulfonic acids produced contain a considerable proportion of oils which were

emulsified and dissolved in the extract. The purification of the sulfonic acids may be performed by the method described for naphthenic acids.

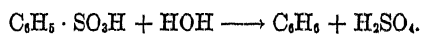
The calculation of the percentage of aromatics in high-boiling fractions by direct determination of the volume loss after treatment with sulfuric acid may give erroneous results due to the solubility of sulfonic acids formed in the treated oil and to the losses which accompany their extraction by water-alcohol. In addition to this, viscous hydrocarbons of the high-boiling fractions may be absorbed by the sludge to a much greater degree than those of gasolines. Thus the final determination of the percentage of aromatics is carried out on the basis of aniline points or other properties of oils before and after treatment with sulfuric acid, as described in Chapter 2.

High-boiling fractions and products which are very viscous or solidified, due to the presence of paraffin wax are diluted with an aromatic-free, low-boiling naphtha (boiling, for instance, between 50° and 80°C) before treatment with sulfuric acid. The ratio of naphtha to oil is from about 3:1 to 5:1.

Regeneration of Aromatics from Sulfonic Acids

This reaction is of some importance for the identification of aromatic hydrocarbons present in narrow fractions of straight-run gasolines as well as of cyclohexanes converted into aromatics by the method of selective dehydrogenation described on page 156. In the last case it is believed that no isomerization takes place during the dehydrogenation.

As is well known,² aromatic sulfonic acids are hydrolyzed in the presence of steam at temperatures above 100°C into hydrocarbons and sulfuric acid, as, for instance:



This reaction is the reverse of sulfonation. Sulfonic acids with dilute sulfuric acid are charged into a flask. The reaction is carried out in the presence of superheated steam, and the hydrocarbons formed are condensed with water. The operation of regeneration may follow immediately the sulfonation reaction. After sulfonation the acid layer is diluted with an equal volume of dilute sulfuric acid (50 per cent) and then steam-distilled.

The hydrolysis of benzene sulfonic acid requires a higher temperature, about 175°C; that of toluene sulfonic acid 150°C; and that of sulfonic acids of higher benzene derivatives 100-130°C. Thus the reaction usually takes place at temperatures from 150 to 170°C. The aromatic hydrocarbons recovered can be oxidized to produce acids of known structure, such as benzoic, phthalic, isophthalic, terephthalic, etc.

The yield of aromatics in the reaction of sulfonic acids with steam is usually fair for such hydrocarbons as toluene, xylenes, ethylbenzene, etc., being as high as 90 per cent of theoretical. According to Carpen-

ter,¹⁵ however, the total recovery of aromatics by this method from gasoline and kerosene fractions was only 60 per cent of the theoretical yield.

Various modifications of this method have been developed. In order to avoid decomposition reactions of sulfonic acids, Smith and Lux¹³⁷ recommended the "flash" system, *i.e.*, sulfonic acids or the paste of sodium sulfonate and water are run slowly into the sulfuric acid. Superheated steam is passed through the sulfuric acid at 145-150°C (in an outside bath) and removes the hydrocarbons formed immediately. Under these conditions, the yield of hydrocarbons is from 80 to 90 per cent of theoretical even from sulfonic acids sensitive to hot sulfuric acid.

A certain degree of separation of aromatic hydrocarbons can be obtained as a result of selective sulfonation and selective hydrolysis. It has been mentioned above that aromatics differ in their ability to be sulfonated, just as sulfonic acids differ in their ability to hydrolyze. White, and Rose¹⁵⁷ described the separation of meta-xylene from the eutectic mixture of meta-xylene and para-xylene. The mixture was sulfonated with 2 volumes of sulfuric acid (1.84) at 0°C for 24 hours. The separated acid was diluted with weak sulfuric acid and steam-distilled at 130-135°C. Nearly pure meta-xylene was then recovered.

It should be also remembered that meta-xylene is commercially separated from other isomers by the same method of selective sulfonation because of its higher capacity to sulfonate as compared with other isomers.

The separation of ethylbenzene and meta-xylene by the same method has been described by the authors cited.¹⁵⁷ Ethylbenzene is less susceptible to sulfonation than meta-xylene. As a result, sulfonation at 0°C gives only partial sulfonation of ethylbenzene. Hydrolysis of the acid at 130-135°C produces mostly meta-xylene and at 155-160°C mostly ethylbenzene. The fraction unattacked by sulfuric acid at 0°C was sulfonated at room temperature (about 30°C) for 48 hours. Hydrolysis of the acid layer gave a small amount of meta-xylene and a greater portion of ethylbenzene which was liberated at 146° to 158°C.

Smith and Cass¹³⁴ developed a method of sharp separation of mesitylene (1,3,5-trimethylbenzene, b.p. 164.6°C) from pseudocumene (1,2,4-trimethylbenzene, b.p. 169.2°C). The mixture is completely sulfonated, and the sulfonic acids formed are precipitated by dilution and separated by filtration. The acids are hydrolyzed with constant-boiling hydrochloric acid at 80°C. The mesitylene sulfonic acid hydrolyzes completely under these conditions, and the mesitylene is recovered by steam distillation at 80°C under reduced pressure. The residue in the distillation flask deposits pseudocumene sulfonic acid unchanged, which is filtered off and then hydrolyzed by steam from 50 per cent sulfuric acid at 135-145°C. This method was applied to the separation of mesitylene and pseudocumene in a gasoline fraction by Mair and Schickltanz.⁸² These authors also separated hemimillene (1,2,3-trimethylbenzene)

from a gasoline fraction, using sulfonation and hydrolysis of the sulfonic acid formed.

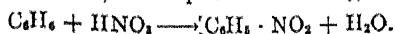
In the above cases, in which the products are simple derivatives of benzene, it is certain that the hydrocarbons recovered by the hydrolysis of sulfonic acids correspond to the original aromatic hydrocarbons before sulfonation. In other cases the structure of the hydrocarbons recovered from the conversion of sulfonic acids may be different from the initial structure. It should be remembered that isomerization and other reactions may accompany the sulfonation. In addition, the yield of hydrocarbons from sulfonic acids of high molecular weight derivatives of benzene, naphthalene, etc., is usually low, due to decomposition reactions. Thus the conclusions made on the basis of the conversion of sulfonic acids frequently may be questionable.

Pilat and Szankowsky¹⁰⁰ regenerated sodium salts of γ - or "green" sulfonic acids into corresponding hydrocarbons. In contrast to the sulfonic acids discussed above, these acids are obtained from high molecular weight hydrocarbons of lubricating oils. The regeneration started at 130°C with superheated steam in the presence of 80 per cent phosphoric acid in the amount equal to that of the sodium sulfonate. The temperature gradually increased to 250°C. The yield of hydrocarbons was about 60 per cent of the sodium sulfonate. The hydrocarbons regenerated were highly aromatic, and had a specific gravity of more than 1.0 and a refractive index of more than 1.6. The authors believe that the hydrocarbons recovered correspond to the original hydrocarbons, which produced the γ -acids on sulfonation. As a proof, the authors sulfonated the regenerated hydrocarbons and converted them into sulfonic acids very similar to the γ -acids. The molecular weight of the regenerated hydrocarbons, however, from 140 to 255 seems to be too low as compared with the original hydrocarbons of lubricating oils.

Nitration

Nitration is a general reaction which can be applied to aromatics, naphthenes and paraffins. The conditions of this reaction, however, are quite different for aromatics and other hydrocarbons. Only aromatic hydrocarbons are nitrated by cold concentrated nitric acid, yielding nitrocompounds almost quantitatively. Under these conditions nitration can be used for quantitative separation of aromatics, at least of the benzene series. Naphthenes and paraffins remain inactive, with the exception of tertiary hydrocarbons, which may be slowly oxidized by cold nitric acid. In any case, no nitrocompounds of paraffins or naphthenes are formed. As will be seen later, the nitration of these hydrocarbons takes place at high temperatures and by dilute nitric acid.

The nitration of aromatics has been used to a much larger extent in petroleum chemistry than that of paraffins and naphthenes. The nitration of benzene, for instance, takes place according to the equation:



Only concentrated nitric acid has a nitrating effect. The reaction is accompanied by formation of water, which dilutes the acid. For this reason, concentrated sulfuric acid is used in the nitrating mixture to bind the water formed. Under the conditions specified below, the nitration of aromatic hydrocarbons produces mostly mononitrocompounds; but the formation of polynitrocompounds to a small extent is also possible.

The nitration of aromatics can be carried out quantitatively, particularly in straight-run gasolines. Determination of aromatics by nitration can be used successfully for narrow fractions containing, for instance, benzene, toluene, etc., by weighing the amount of the nitrocompound formed. Nitrobenzene or nitrotoluene is dissolved in an excess of nitrating mixture and separated by dilution of the mixture with water. The determination is based on the assumption that only mononitrocompounds are formed.

The nitration of total gasoline produces various nitrocompounds of unknown molecular weight so that the weight of nitrocompounds formed does not indicate the amount of aromatic hydrocarbons reacted. In such cases the loss in the volume of gasoline due to the nitration of aromatics may be used for determining aromatics present in the gasoline and nitrated. As has been mentioned, the nitrocompounds formed are dissolved in nitrating mixture and are almost completely removed from the aromatic-free gasoline. It is understood that this method can also be used for determining benzene or toluene in corresponding narrow fractions.

The analysis is carried out as follows.⁴⁸ A certain volume of gasoline of about 100 cc is mixed with three volumes of sulfuric acid (1.84) under cooling in an ice bath. To this mixture the nitrating mixture is gradually added, with stirring or shaking, in an amount approximately equal to the weight of the gasoline, if the proportion of aromatics does not exceed 25 per cent. Otherwise, the amount of the nitrating mixture is correspondingly increased. The nitrating mixture consists of one part nitric acid (1.42), freed of nitrous acid by blowing with air at 40°-45°C, and two parts sulfuric acid (1.84). Addition of the nitrating mixture is carried out drop by drop under continuous cooling. After the nitration is completed, two and a half more volumes of sulfuric acid are added; the mixture is shaken, and after standing for 3 hours the volume of the unreacted gasoline is measured. The difference between the initial volume and that after the nitration equals the volume of aromatics present in the original gasoline. The correction $1.7 \times N/100$, corresponding to the solubility of non-aromatic hydrocarbons in sulfuric acid is added to the volume of the unreacted gasoline, N being the number of cc in the sample.

Hess recommends nitrating in a special flask with a graduated neck. The flask is provided with a glass stopper and a funnel for introducing the nitrating mixture. The reaction is performed with shaking. When the reaction is completed, an excess of sulfuric acid is added to displace the gasoline unreacted to the graduated neck of the flask.

The method described usually gives reliable results. However, it can

from a gasoline fraction, using sulfonation and hydrolysis of the sulfonic acid formed.

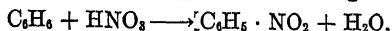
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The nitration of total gasoline produces various nitrocompounds of unknown molecular weight so that the weight of nitrocompounds formed does not indicate the amount of aromatic hydrocarbons reacted. In such cases the loss in the volume of gasoline due to the nitration of aromatics may be used for determining aromatics present in the gasoline and nitrated. As has been mentioned, the nitrocompounds formed are dissolved in nitrating mixture and are almost completely removed from the aromatic-free gasoline. It is understood that this method can also be used for determining benzene or toluene in corresponding narrow fractions.

The analysis is carried out as follows.⁴⁸ A certain volume of gasoline of about 100 cc is mixed with three volumes of sulfuric acid (1.84) under cooling in an ice bath. To this mixture the nitrating mixture is gradually added, with stirring or shaking, in an amount approximately equal to the weight of the gasoline, if the proportion of aromatics does not exceed 25 per cent. Otherwise, the amount of the nitrating mixture is correspondingly increased. The nitrating mixture consists of one part nitric acid (1.42), freed of nitrous acid by blowing with air at 40°-45°C, and two parts sulfuric acid (1.84). Addition of the nitrating mixture is carried out drop by drop under continuous cooling. After the nitration is completed, two and a half more volumes of sulfuric acid are added; the mixture is shaken, and after standing for 3 hours the volume of the unreacted gasoline is measured. The difference between the initial volume and that after the nitration equals the volume of aromatics present in the original gasoline. The correction $1.7 \times N/100$, corresponding to the solubility of non-aromatic hydrocarbons in sulfuric acid is added to the volume of the unreacted gasoline, N being the number of cc in the sample.

Hess recommends nitrating in a special flask with a graduated neck. The flask is provided with a glass stopper and a funnel for introducing the nitrating mixture. The reaction is performed with shaking. When the reaction is completed, an excess of sulfuric acid is added to displace the gasoline unreacted to the graduated neck of the flask.

The method described usually gives reliable results. However, it can

be applied only to straight-run gasolines not containing any unsaturates which also react with nitric acid.

Egloff and Morrell²⁷ developed another modification of the nitration method for determining the percentage of aromatics. They treat gasoline with a nitrating mixture containing 25 per cent of nitric acid, 58 per cent of sulfuric acid, and 17 per cent of water; 20 cc of gasoline are treated with 50 cc of the nitrating mixture. The authors claim that the nitrocompounds formed are not dissolved in such a nitrating mixture, but cause the formation of a layer, which is determined. The operation requires from 15 minutes to an hour. After standing, the nitrocompounds form an intermediate layer between the acid at the bottom and the oil layer on top. The number of cc of the nitrocompounds is multiplied by the factor 4.3 to obtain the percentage of aromatics in the gasoline of 410°F.

Faragher, Morrell, and Levine³⁰ found, however, that the value of the factor depends on the concentration of the aromatics, as well as on their nature. Thus the Hess method should be preferred to the determination of the volume of nitrocompounds formed in view of the variability of the factor relating the concentration of aromatics to the volume of nitrocompounds.

As stated above, nitration of aromatic hydrocarbons is frequently employed for the purpose of separation. The nitrocompounds formed, or the amines produced by reduction of the nitrocompounds may be identified in few cases. Some aromatics form under certain conditions crystalline trinitrocompounds which may be identified and in some cases quantitatively separated (*e.g.*, trinitromesitylene almost insoluble in acetone^{111c}).

Nitration under the above conditions has been applied mostly to aromatic hydrocarbons boiling in the range of gasolines. The high molecular weight aromatics are also easily nitrated under the same conditions, producing heavy, non-crystallizable liquids, but the structure of such nitrocompounds is entirely unknown.

Nitration is not used for the separation and identification of paraffins and naphthenes to any large extent. Concentrated cold nitric acid does not affect normal and quaternary paraffins, but it oxidizes paraffins with a tertiary carbon atom. Various monobasic and dibasic acids, as well as carbon dioxide, are formed; hence identification of the initial hydrocarbons is practically impossible on the basis of the reaction products. Nitration of paraffins and naphthenes is carried out at 130-140°C in sealed tubes with dilute nitric acid (Konovalov). The reaction is not quantitative. Secondary and tertiary nitrocompounds are formed, the identification of which is possible only for some simple compounds of this class. Markovnikoff nitrated such paraffins as 2-methylpentane and 2,2-dimethylpentane to yield nitrocompounds which could be identified.^{88, 89}

Nitration of normal paraffins forms secondary nitrocompounds soluble in alcohol caustic solution, whereas tertiary nitrocompounds produced by nitration of isoparaffins are insoluble in this reagent (Konovalov⁷¹).

Thus, separation and identification of normal and isoparaffins is possible by this method. The application of the nitration method to high molecular weight compounds like paraffin wax and ceresin will be described in Chapter 6.

Grundman⁴⁰ described the nitration of paraffins of a higher molecular weight under atmospheric pressure at temperatures from 150 to 200°C. The superheated vapor of nitric acid is injected into heated liquid hydrocarbons. As in the case of Konovalov's method, nitration is slow, and requires from two to five hours. Primary, secondary and tertiary nitrocompounds are formed. A portion of the hydrocarbons is oxidized into fatty acids, ketones, and carbon dioxide. Nitration of paraffins in vapor phase has been discovered and developed by Hass and his co-workers.^{9, 26, 43-46, 49, 131} The nitration mixture of a hydrocarbon and vaporized nitric acid or nitrogen dioxide is passed into a reaction chamber at temperatures from 300 to 500°C. The reaction is very rapid and gives a mixture of various isomeric nitrocompounds. In addition, nitrocompounds of low molecular weight hydrocarbons are formed as a result of decomposition. Thus, nitration of normal pentane gives 1-, 2-, and 3-nitropentanes, nitropropanes, nitroethane and nitromethane. Some fatty acids may also be formed. The method can be applied to paraffins from C_1 to C_{12} . The higher paraffins are completely decomposed, and yield low molecular weight nitrocompounds. This reaction, highly important and used on commercial scale, apparently cannot be applied successfully to the identification of paraffins because of the numerous isomers and low molecular weight nitrocompounds produced by nitration.

Nitration of some naphthenes was used to a certain extent by earlier workers. Application of this method to the aromatic-free fractions (48-51°C and 70°C) of a Baku gasoline produced nitrocyclopentane and nitromethylcyclopentane, which were reduced to amines. The properties of the amines corresponded to those synthesized from pure hydrocarbons (Markovnikoff;⁸⁷ Markovnikoff and Konovalov⁹¹).

It is of interest to notice that the nitration of paraffins and naphthenes for separation and identification has not been used to any extent in recent years.

Removal of Aromatics with Picric Acid

Picric acid reacts with aromatic hydrocarbons, particularly polyaromatic, forming crystalline compounds containing one mole of picric acid per one mole of the aromatic hydrocarbon. These picrates are almost insoluble in cool hydrocarbons and thus can be separated by filtration.

Picric acid can be used for the separation of aromatic hydrocarbons either in solution, *e.g.*, in ether, or in pure form, the latter being preferable. If pure acid is used, one part of picric acid is dissolved in 100 parts of a petroleum fraction by heating on a steam bath until the acid is completely dissolved. The solution is slowly cooled to 0°C, and the crystals

formed are separated by filtration. The cooling must be very slow; otherwise, at least a part of the picric acid crystallizes free, and does not combine with the aromatics. The operation described is repeated with the filtrate from 5 to 10 times until all the aromatics are removed and until pure picric acid crystallizes from the solution. It should be mentioned that the solubility of picric acid in petroleum fractions (on heating) depends on the percentage of aromatics. Thus the proportions of picric acid used in the repeated operations decrease with decreasing percentage of aromatics because of the gradual removal of the latter.

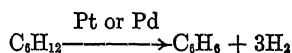
The picrates formed with aromatics are purified by crystallization from ethyl alcohol. They usually have some other color than picric acid, and widely different melting points, which are frequently used for identification of aromatics. Recovery of aromatic hydrocarbons from picrates is carried out by reaction with weak ammonia and steam distillation, at least for the derivatives of naphthalene, which are easily volatile with steam.

Cosciug¹⁸ found that separation of naphthalene derivatives (naphthalene, methylnaphthalenes, di- and trimethylnaphthalenes) from narrow fractions may be performed successfully by the method described. Further separation of isomers by fractional crystallization of picrates, however, turned out to be impractical.

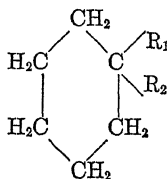
It is rather surprising that this method of separating aromatics so far has been used to a very limited extent. The selectivity of the method in question is very high and it is easy to carry out.

Determination of Cyclohexanes

Gasolines, both straight-run and cracked, treated with an excess of sulfuric acid and redistilled (if necessary), contain only paraffins and naphthenes. The derivatives of cyclohexane can be separated from other hydrocarbons, *i.e.*, from paraffins and derivatives of cyclopentane, by catalytic dehydrogenation into aromatic hydrocarbons which are then separated with sulfuric acid. Catalytic dehydrogenation of cyclohexanes in the presence of platinum or palladium catalysts was discovered by Zelinsky.^{16a}

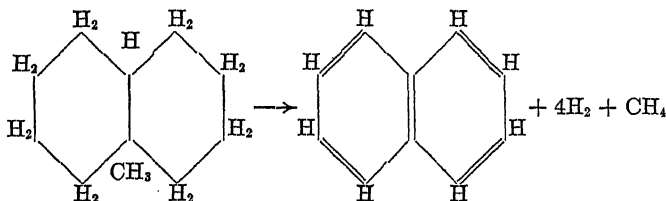


He showed that this reaction, conducted at moderate temperatures (about 300°C), converts cyclohexanes quantitatively and selectively into aromatic hydrocarbons of the same structure. Other hydrocarbons, *e.g.*, paraffins and cyclopentanes, are not affected under the conditions, to be specified later. Dehydrogenation of cyclohexanes in the presence of heterogeneous catalysts is performed in one stage, without formation of partially dehydrogenated cyclohexanes, *i.e.*, cyclohexenes. As shown above, the reaction produces three molecules of hydrogen. Therefore, the cyclohexane derivatives of the structure



as, for instance, 1,1-dimethylcyclohexane are not dehydrogenated. In contrast to these quaternary derivatives, all mono-alkylcyclohexanes or polyalkylcyclohexanes of tertiary structure are easily dehydrogenated, forming three molecules of hydrogen, according to the equation given above. This should be kept in mind when the method in question is applied to gasoline fractions. The investigation of the National Bureau of Standards (Chapter 4) shows that the cyclohexane derivatives of the type which is not convertible to aromatics may be present in gasoline fractions, at least in comparatively small amounts.

It should be pointed out, however, that the passivity of quaternary structures to catalytic dehydrogenation cannot be considered as a general phenomenon and is apparently confined mostly to the derivatives of cyclohexane. Decalin derivatives with quaternary carbon atoms, as well as other polycyclic hydroaromatic hydrocarbons of the same structure, can be catalytically dehydrogenated, as has been shown by Linstead and his co-workers⁷⁶ and by Ruzicka and Waldmann.¹²¹ Dehydrogenation of such structures produces not only the dehydrogenation effect but also the splitting of an alkyl group in the form of a hydrocarbon, as, for instance:



These reactions may be accompanied by a partial shift of the methyl group to another position in the ring, which, however, is usually of subordinate importance compared with the principal reaction given above. Both naphthalene and β -methylnaphthalene may be formed as a result of the dehydrogenation and the shift.

Zelinsky, Kasansky, and Plate¹⁰⁸ found later that cyclopentane and its derivatives are transformed into open-chain paraffin hydrocarbons in the presence of platinized charcoal and hydrogen at 305 to 315°C. This reaction, however, takes place only in the presence of an excess of hydrogen and thus does not interfere with the dehydrogenation of cyclohexanes under the conditions of the method. Aromatics are not formed from cyclopentanes under these conditions.

Another possible side reaction is the catalytic dehydrogenation of paraffins into olefins. Tausz and von Putnok¹⁴¹ found that olefins are

actually formed from paraffins in the presence of highly active catalysts at temperatures close to 300°C. The extent of this reaction was, however, very slight, and it did not affect the analytical results appreciably. On the other hand, suppression or complete elimination of the formation of olefins is very important, since the activity of the catalyst is greatly impaired by olefins and their polymerization products which form upon it. The formation of olefins progresses rapidly with increasing temperature. Thus it is important to dehydrogenate cyclohexanes at lower temperatures (about 270-280°C), 300°C being the maximum permissible. The use of temperatures lower than 270°C is practically impossible in view of very slow reaction rates at these temperatures. The method of dehydrogenating cyclohexanes can be applied to the fractions boiling below 200°C. Even dehydrogenation of the fractions boiling between 150-200°C frequently involves some difficulties. Dehydrogenation of fractions boiling above 200°C is very slow, and is accompanied by side reactions which affect the activity of the catalyst. Platinum or palladium catalysts should be preferred to nickel. In the presence of the latter, the rate of dehydrogenation is slower, and side reactions occur to a greater extent.

Platinum and palladium catalysts are deposited on such carriers as asbestos or charcoal. The preparation of the catalyst is as follows: 15 to 20 gr. of platinum or palladium chloride are dissolved in a small amount of water slightly acidulated with hydrochloric acid. The solution is mixed with 100 cc of formalin (40 per cent formaldehyde). The asbestos or charcoal is impregnated with the mixture, and then 100-120 cc of a strong (50 per cent) solution of potassium hydroxide are added to the asbestos drop by drop at 0°C. The reaction is finished on a steam bath at 50°C for 30 minutes. The metallized asbestos or charcoal is washed with weak acetic acid and water and then dried at 110°C. The catalyst must contain at least 20 per cent of metallic palladium or platinum; still higher concentrations of the metals are beneficial.

The poisoned and inactive catalyst may be regenerated by oxidation in air at 250°C for two hours and by subsequent reduction with hydrogen. The initial activity of the catalyst, however, is not completely restored after regeneration. Complete regeneration is brought about by dissolution of the metal in aqua regia. The solution is evaporated completely, the residuum is dissolved in water, and the solution obtained is reduced by hydrazin hydrochloride. The reduced metal is repeatedly dissolved in aqua regia and used for the preparation of the catalyst, as described above.

If a nickel catalyst is used for dehydrogenation of cyclohexanes, it is supported on alumina or activated charcoal.¹⁶⁸ The percentage of nickel with respect to alumina must not exceed 20 per cent. Such a catalyst is predominantly dehydrogenating at temperatures below 300°C, and does not cause undesirable side reactions, particularly decomposition of hydrocarbons to carbon, methane and hydrogen to any appreciable extent.

The apparatus for dehydrogenation consists of a glass tube 80-100 cm

long and about one cm wide. The tube is placed in an electric oven which is 20 cm shorter than the tube. The latter is filled with the catalyst, which occupies only the heated part of the tube. The inlet of the tube is connected with a graduated burette which serves as a container for the product to be dehydrogenated. The outlet end of the tube is connected with a cooler and then with a receiver of about 50 cc capacity, cooled to -40°C . The receiver has a connection with a gas burette for measuring the hydrogen formed by dehydrogenation. The inlet of the tube is also connected with a source of highly purified and dry hydrogen, which is used before the experiment on heating the catalyst to the temperature required (270 - 300°C).

Selective dehydrogenation of cyclohexanes at moderate temperatures (up to 300°C) is a rather slow process. The rate corresponds to 2-3 cc of the product to be dehydrogenated per hour. Even under these conditions the reaction is incomplete. Thus the procedure is repeated with the partially dehydrogenated product (condensate) several times, usually three or four. When dehydrogenation is complete, the formation of hydrogen stops and the refractive index (or specific gravity) of the condensate remains unchanged. The temperature of dehydrogenation may be increased to 350°C , if the reaction is used only for identification of the hydrocarbon. Under these conditions, however, the yield of the aromatic is much less than theoretical due to side reactions.

A completely dehydrogenated product is treated with sulfuric acid to remove the aromatic hydrocarbons formed. The percentage of these is determined on the basis of refractive index or aniline points before and after dehydrogenation. The amount of hydrogen formed on dehydrogenation may be used for controlling the results obtained by the above methods.

Yuriev and Zhuravlev¹⁶⁴ discussed the application of the dehydrogenation method to the determination of cyclohexanes and cyclopentanes in straight-run gasolines. The accuracy of the quantitative determination of cyclohexanes by the dehydrogenation method is very satisfactory, provided the catalyst used remains sufficiently active. Petroleum products and fractions containing a considerable percentage of sulfur compounds poison the catalyst rapidly. This may involve considerable error in the determination of cyclohexanes. Otherwise, the accuracy of the method is about 2-3 per cent of the total amount of cyclohexanes.

As previously mentioned, catalytic dehydrogenation can be used for the identification of cyclohexanes separated from petroleum. For instance, White and Glasgow¹⁵⁶ identified a nononaphthene as 1,2,4-trimethylcyclohexane by dehydrogenation of the hydrocarbon over palladized asbestos (20 per cent of palladium). A 5-cc charge of the nononaphthene, having a refractive index of 1.4229, was dehydrogenated at the rate of six drops per minute in a tube containing a 50-cm section of the catalyst at 340 to 380°C . The passage required 25 minutes. A product in the amount of 3.2 cc was obtained, which had a refractive index

1.4827 and which was impure 1,2,4-trimethylbenzene. The product was sulfonated and then hydrolyzed by steam distillation, which gave 1.3 cc of a hydrocarbon with a refractive index of 1.5022 (1.5017 for 1,2,4-trimethylbenzene).

As described above, the dehydrogenation of cyclohexanes is carried out in the vapor phase. Some polycyclic hydrocarbons containing cyclohexane rings can be dehydrogenated in the liquid phase. Linstead and his co-workers⁷⁶ dehydrogenated tetralin to naphthalene by boiling over a platinum or palladium catalyst as well as alkyltetralins without a quaternary carbon atom.⁷⁷ However, the reaction in the liquid phase is not general, since, *e.g.*, decalin is not dehydrogenated on boiling but is easily dehydrogenated in the vapor phase (Zelinsky's method) at higher temperatures (about 300°C).

The method of dehydrogenating hydroaromatic hydrocarbons by elemental sulfur or selenium must not be ignored. Ruzicka and Meyer¹¹⁹ and Ruzicka, Meyer and Mingazzini¹²⁰ successfully applied this method (dehydrogenation by sulfur) to hydrogenated naphthalenes and terpenes, transforming them into corresponding aromatic hydrocarbons. A hydrocarbon is treated with the theoretical amount of sulfur for several hours at from 200 to 300°C until formation of hydrogen sulfide ceases. The reaction product is then distilled, and the aromatic hydrocarbon formed is refractionated. For some hydrocarbons containing cyclohexane rings the dehydrogenation by sulfur is practically quantitative.

Diels and his co-workers^{24, 25} dehydrogenated cyclic hydrocarbons containing cyclohexane rings with selenium. The reaction is similar to that with elemental sulfur and is accompanied by the formation of hydrogen selenide. The process with selenium is carried out at somewhat higher temperatures (up to 350°C).

Another promising method of dehydrogenating six-member naphthenes into aromatics has been recently developed by Adkins, Richards and Davis.¹ Hydroaromatic hydrocarbons, including the derivatives of polycyclic condensed naphthenes, are dehydrogenated into corresponding aromatics at 300-350°C in the presence of benzene over a nickel or platinum catalyst. Under such conditions, benzene is hydrogenated, as it is a hydrogen acceptor. The treatment does not change the structure of the paraffinic side chains.

The dehydrogenation methods are used only for investigation, qualitative and quantitative, of the cyclic structure of hydrocarbons. The importance of the methods in question is due to the fact that the cyclic hydrocarbons represent the bulk of the crude oils and of the synthetic crudes produced by cracking. Six-member saturated rings are transformed into aromatic rings, which are much better known and more easily identified than any other cyclic hydrocarbons. The dehydrogenation of paraffins into olefins is also quite feasible, but useless from the analytical standpoint, since the identification of olefins would be much more difficult than that of paraffins.

There are limitations to the application of the dehydrogenation methods. In some cases the dehydrogenation of six-member saturated rings is very slow at moderate temperatures, or requires such high temperatures that several side reactions would take place. Thus, although the successful dehydrogenation of a hydrocarbon or a narrow fraction to an aromatic is proof of the six-member ring structure of the initial hydrocarbon, the negative result of the reaction seems to be insufficient to rule out the structure in question. The absence of the reaction might be due to the inactivity of the hydrocarbon. The conclusions on the basis of negative results of the dehydrogenation of monocyclic naphthenes boiling in the range of gasoline are more reliable, since the six-member ring naphthenes boiling in this range are dehydrogenated under moderate temperatures without difficulty.

Any conclusions on the position of paraffinic side chains in the original cyclohexane rings seem to be open to question because of the possible shift of the chains, as previously mentioned. For various homologs of cyclohexane such shifts were not observed, however.

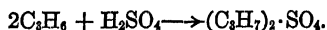
It should be also kept in mind that under certain conditions the catalytic dehydrogenation of paraffins may produce the cyclization effect, with resulting formation of aromatics. Kasansky and Plate⁶² observed the formation of aromatic hydrocarbons from normal octane, diisobutyl and diisoamyl over a platinum catalyst in small yields. The production of aromatic hydrocarbons by cyclization of normal and isoparaffins at high temperatures over a chromia catalyst is a well known semi-commercial process. The cyclization of paraffins into aromatics, however, does not seriously affect the application of dehydrogenation methods to petroleum hydrocarbons in view of the specific conditions required for cyclization of paraffins, as well as of the specific nature of paraffins, which are easily convertible into aromatics and which are absent in naphthenic hydrocarbons or fractions to be dehydrogenated.

Reactions and Separation of Unsaturated Compounds with Sulfuric Acid

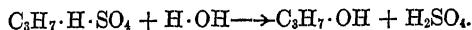
The reactions between unsaturated compounds and sulfuric acid are much more complicated than in the case of aromatic hydrocarbons. The reactions of olefins of various molecular weight were thoroughly investigated by Brooks and Humphrey,¹⁸ Norris and Joubert,¹⁰⁵ and others. In the presence of sulfuric acid olefins may form esters, alcohols, and polymers. The main factors determining the reaction are the molecular weight of olefins, their structure, the concentration of sulfuric acid, and temperature. The olefins of a lower molecular weight, such as ethene or propene, readily form an ester of sulfuric acid:



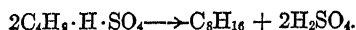
In the presence of an excess of olefin, dialkyl esters are formed:



If the acid is rather dilute, the ester formed may be hydrolyzed to an alcohol:



Brooks and Humphrey, however, pointed out that formation of alcohols is possible without the intermediate formation of esters. The esters formed by higher molecular weight olefins are easily converted into polymers, as, for instance:



The formation of esters as intermediates in polymerization of low molecular weight olefins seems very probable. The mechanism of polymerization of high molecular weight olefins, however, is unknown, and the intermediate formation of esters for such olefins has not been proved.

Olefins from C_2 to C_7 may yield both alcohols and polymers, depending on their structure, the concentration of the acid, and the temperature. An elevated temperature and high concentration of sulfuric acid favor the formation of polymers. For instance, treating butenes and isobutene with sulfuric acid (60 per cent or higher) at 100°C gives a quantitative yield of polymers, mostly dimers. Isoolefins are more easily polymerizable than normal olefins. Octenes and olefins of a higher molecular weight almost always yield polymers, independently of the conditions of treatment. The dimers and polymers formed are more resistant to sulfuric acid than the original olefins. As a result, the formation of high molecular weight polymers does not take place to a great extent. Some olefins, such as hexadecene, form chiefly dimers.

The dimers and polymers formed on treatment with sulfuric acid are insoluble in an excess of acid and completely soluble in the oil treated. As a result, they remain in the oil. Thus, according to Brooks and Humphrey, the polymers are separated by distillation as bottoms from unreacted constituents of the oil. "The volume of the heavily polymerized residue, plus the loss to the acid, equals approximately the volume percentage of olefins originally present." Olefins are attacked by sulfuric acid more easily than aromatics. Thus dilute sulfuric acid may frequently be used for the reaction with low molecular weight olefins, particularly for producing alcohols.

Tilicheyev and Massine¹⁴⁴ investigated the reaction of a cracked fraction, boiling from 50 - 100°C , obtained on cracking paraffin wax, with sulfuric acid of varied concentration. This fraction contains mostly paraffins and olefins. The results are given in Table 45.

The reactivity of olefins with sulfuric acid depends upon their molecular weight or boiling temperature, as the data of the authors cited clearly show (Table 46).

The results included in Tables 45 and 46 indicate that 85-90 per cent sulfuric acid may remove olefins from low boiling gasolines almost completely, particularly after two repeated treatments. It is understood that

the treatment is followed by redistillation up to the final boiling point of the original fraction or gasoline to remove the polymers formed. This is the weakest point of the method, however. Distillation of the original gasoline or fraction to the end point leaves a certain amount of residue or bottoms of distillation. This residue is subtracted from the residue obtained on distillation after treatment with sulfuric acid, on the assumption that the distillation curves are additive. An appreciable error may be involved in this simplification. The error, however, might be comparatively small for gasolines containing a large proportion of unsaturates and forming a correspondingly high percentage of polymers.

Table 45. Action of sulfuric acid of various concentrations on the 50° to 100°C fraction obtained after cracking paraffin wax. Treating conditions: one volume of sulfuric acid per one volume of fraction, shaking for 30 minutes with cooling.

Concentration of H_2SO_4 (%)	Iodine number of fraction after treatment and redistillation	Olefins removed (%)
0 (original fraction)	153.2	0.0
80	77.7	49.3
85	24.1	84.3
85 (two treatments)	13.9	90.9
90	1.4	99.1
95.6	0.17	99.9
Fuming	0.07	100.0

Table 46. Influence of the boiling temperature of fractions obtained after cracking paraffin wax on the reaction of olefins with sulfuric acid followed by redistillation. Treating conditions: same as in Table 45.

Concentration of H_2SO_4 (%)	Fraction, Boiling range (°C)	Olefins removed (%)
80	50-100	49.3
80	100-150	20.5
85	50-100	84.3
85	100-150	74.7
85	150-200	35.6

The formation of esters, alcohols and polymers by treatment of olefins with sulfuric acid are the most important reactions effected by this reagent. In many cases the conditions (temperature, concentration of sulfuric acid, etc.) can be controlled closely enough to produce one of the above products in an almost quantitative yield. In addition to these principal reactions, however, many side reactions are possible, which lead to the formation of paraffins, cyclic hydrocarbons and highly unsaturated or tarry substances. Nametkin, Abakumovskaya and Rudenko^{88, 89} found that the polymers formed are partially dehydrogenated to highly unsaturated hydrocarbons by the further action of sulfuric acid. The hydrogen liberated is quantitatively consumed by another part of the polymer, with formation of saturated hydrocarbons, *i.e.*, hydrogenated dimers, trimers, etc. The highly unsaturated hydrocarbons formed are dissolved in sulfuric acid and may be further condensed into tars.

Very little is known of the reactions between other unsaturated hydrocarbons and sulfuric acid.

Cyclic olefins, *e.g.*, cyclohexene, are affected by strong sulfuric acid, apparently in the same manner as aliphatic olefins. Nametkin and Abakumovskaya⁹⁷ showed that treatment of cyclohexene with concentrated sulfuric acid yields polymers as well as saturated hydrocarbons.

The reaction of styrene and diolefins with sulfuric acid is much more violent and is accompanied by marked increase in temperature. The primary reaction is probably polymerization. The polymerization of diolefins under controlled conditions (low temperature and/or a small proportion of a catalyst) may be a predominant reaction, but in the presence of an excess of sulfuric acid it is followed by the secondary reactions mentioned above to a much greater extent than with olefins. As a result, the formation of tarry substances may be almost quantitative.

Brooks and Humphrey¹⁸ pointed out that the formation of tars on treating petroleum products with sulfuric acid is due either to diolefins or to condensation reactions of olefins with aromatics.

Thus all unsaturated hydrocarbons react more or less vigorously with sulfuric acid, giving various products, such as esters, alcohols, polymers, highly unsaturated hydrocarbons, paraffins and other saturated hydrocarbons, and tars. Some of these products (esters, alcohols, highly unsaturated hydrocarbons and tars) are miscible with sulfuric acid and are withdrawn with excess sulfuric acid and sludge formed. Others, *i.e.*, polymers and saturated hydrocarbons, are dissolved in the hydrocarbon layer and can be separated more or less quantitatively by redistillation up to the end point of the original product or fraction, since the polymers have in general a higher boiling point than the original fraction. This separation, however, is possible only for comparatively low-boiling fractions, including gasoline, naphtha and kerosene fractions. For higher-boiling fractions the determination of the end point does not give any reliable results.

The reaction of gaseous unsaturates over phosphoric acid takes place at higher temperatures and pressures (above 100°C and at 10-20 atmospheres) and yields polymers. The mechanism of this reaction is essentially the same as with sulfuric acid. This reaction, widely used commercially, has not been applied to the separation of unsaturates from gasolines because of the experimental complications involved in the use of high pressures and temperatures. Nevertheless, selective polymerization of unsaturates with phosphoric acid may have a certain advantage over that with sulfuric acid, since the reactions involving other hydrocarbons, *i.e.*, aromatics and tertiary paraffins, may be completely eliminated under certain conditions.

Recently Hoog and Eichwald⁵⁸ reported on a new method of selective separation of unsaturates with the aid of thioglycolic acid, which forms acidic compounds with unsaturates. The reaction takes place for 16 hours at room temperature in propionic acid solution with an excess of thioglycolic acid. The compounds formed are removed from the hydro-

carbons unreacted by washing with alcoholic caustic solution. The separation of unsaturates is reported to be complete.

Separation of Unsaturates and Aromatics with Sulfuric Acid

Many workers have tried to use the difference in the reactivity of olefins and aromatics toward sulfuric acid for selective separation of olefins and other unsaturates from aromatic hydrocarbons in cracked gasolines containing both classes of hydrocarbons. Egloff and Morrell²⁷ suggested using 80 per cent sulfuric acid, Ormandy and Craven¹⁰⁶ 88 per cent, Riesenfeld and Bandte^{6, 112, 113} 85 to 92 per cent at 0°C. It has been assumed that, under the conditions specified, only olefins react with sulfuric acid and that aromatics are not affected.

Recently, Fisher and Eisner³² recommended treating the oils successively with sulfuric acid in gradually increasing concentrations from 80 to 98 per cent and determining each time the volume, specific gravity and refractive index of the residual oil. The specific gravity or refractive index (or, better, specific refraction or refractive intercept) are plotted versus the volume of residual oil. In the first stages chiefly olefins are extracted, increasing the specific refraction or refractive intercept. Then the aromatics become involved in the reaction, decreasing this function to the constant value corresponding to the total removal of aromatics. The authors believe that the maximum value of the intercept corresponds to the total removal of unsaturates.

As the data of Tables 45 and 46 show, however, the reaction of olefins with 80-85 per cent sulfuric acid is far from complete, particularly with olefins of high molecular weight. As a result, the content of olefins determined with weak sulfuric acid may be much lower than actual. On the other hand, sulfuric acid of higher strength (88-92 per cent) readily attacks aromatic hydrocarbons, with the exception of benzene.

In addition, Brochet,¹² Brame,¹⁰ Ormandy and Craven,¹⁰⁶ and Tiliheyev and Massine¹⁴⁵ showed that aromatics are condensed with olefins in the presence of sulfuric acid even if the concentration of the acid is comparatively moderate (85 to 93 per cent). As a result, the selectivity of dilute sulfuric acid toward olefins is even less than might be expected on the basis of the reactions discussed in the foregoing section.

If selective removal of unsaturates with sulfuric acid is not feasible, this reaction can be used for determining the total content of unsaturates and aromatics. One volume of cracked gasoline is treated with 3 volumes of 96-98 per cent sulfuric acid for one hour. The loss of gasoline to the sludge after treatment and standing is recorded. The treated gasoline is washed, neutralized, dried, and distilled to the end point of the original gasoline, to determine the amount of high molecular weight polymers formed. The amount of distillation residue of the original gasoline is subtracted from the amount of bottoms. The total amount of unsaturates and aromatics equals the loss to the acid plus the amount of bottoms

after redistillation, recalculated on the corrected amount of gasoline left after treatment with sulfuric acid. The iodine number of the redistilled gasoline must be zero or very low, indicating complete removal of unsaturates.

Faragher, Morrell and Levine³⁰ recommend the following modification of this method. They shake 100 cc of the gasoline with 3 volumes of 91 per cent sulfuric acid for 30 minutes. The sludge is withdrawn, and the gasoline is distilled to a point 5° above the former end point of the gasoline to separate the unchanged hydrocarbons from the polymers formed in the acid treatment. Finally, the distillate is shaken with 3 volumes of 98 per cent sulfuric acid to remove the olefins and aromatics that escaped the previous treatment. The total reduction in volume represents the unsaturated and aromatic hydrocarbons in the original gasoline. Redistillation after the second treatment is not necessary, as only a relatively small proportion of olefins remains after the first treatment. A preliminary partial removal of unsaturates with 91 per cent sulfuric acid eliminates the possibility of the condensation of aromatics and unsaturates, which may occur if these compounds are removed in one stage.

It should be mentioned that treatment of cracked gasolines with concentrated sulfuric acid must be carried out with necessary precautions, because of the high thermal effect of the treatment. Sulfuric acid is added to gasoline gradually, and the mixture is cooled. Some highly unsaturated gasolines, as for instance, those cracked in the vapor phase, may explode if the precautions mentioned are neglected.

Determination of the total percentage of aromatics and unsaturates can be carried out by the method in question for cracked gasolines and kerosenes. For high-boiling cracked distillates the application of this method encounters the difficulty of redistilling the treated oil to the end point of the original oil. The method so far has not been applied to high-boiling products and fractions. Allen and Duckwell^{1*} absorb aromatics and unsaturates by 4,3 and 2 volumes of 101% sulfuric acid and extrapolate the absorption for zero volume of the acid. The results are claimed to be satisfactory for aromatics and too low for aromatics and unsaturates, as could be expected.

Separation of Aromatics and Unsaturates with Nitric Acid

Garner³⁶ suggested using fuming nitric acid for the total removal of aromatics and unsaturates from gasolines. Aromatics are nitrated, and the nitrocompounds formed are dissolved in an excess of nitric acid. Unsaturated hydrocarbons are oxidized by fuming acid into carbon dioxide, water and acids soluble in an excess of nitric acid. The formation of nitro- and hydroxy-nitrocompounds by nitration of olefins may occur to a slight extent, but not with excess nitric acid, which oxidizes them more or less completely.

The procedure is carried out at -10°C by gradually pouring 50 cc of

the gasoline into 125 cc of fuming nitric acid which has been previously cooled to -10°C . The mixture is continuously shaken during the addition. After the final addition and shaking, the spent nitric acid is separated. The gasoline is then washed three times with 20 cc of fuming acid with vigorous shaking, to remove any dissolved nitrocompounds. After the separation of nitric acid, the gasoline is washed thoroughly with soda solution and water for determination of the aniline point. The volume of the treated gasoline is measured before washing with soda solution. The difference between the original volume of the gasoline (50 cc) and that after the treatment equals the total amount of aromatics and unsaturates present in cracked gasoline.

The method apparently gives fairly reliable results. Tilicheyev and Massine,¹⁴⁵ however, found that fuming nitric acid attacks naphthenes to a certain extent. As a result, the total amount of aromatics and unsaturates determined by the method may be somewhat exaggerated.

Manning⁸⁵ described another modification for the total removal of aromatics and unsaturates with nitric acid. A nitrating mixture is used, consisting of 10 per cent nitric acid (1.4) or 16 per cent of potassium nitrate in 98 per cent sulfuric acid. Two kali-apparatus containing the above nitrating mixture are employed for the analysis. A gasoline sample is placed in a U-tube, connected with the two kali-apparatus, and slowly evaporated in a current of dry air. The weight of gasoline is from 0.2 to 0.5 gram. The total procedure requires from 2 to 8 hours. All aromatic and unsaturated hydrocarbons are absorbed in the first apparatus, and the increase in the weight of this apparatus, corrected in the manner to be described, gives the total amount of aromatic and unsaturated hydrocarbons in the sample. The second kali-apparatus is used to determine the amount of saturated hydrocarbons absorbed by nitric mixture. This amount is subtracted from the weight of the hydrocarbons absorbed in the first kali-apparatus. As stated above, the removal of unsaturated and aromatic hydrocarbons with nitric acid is feasible only for gasoline fractions.

The National Bureau of Standards in the investigation of the chemical composition of petroleum frequently used nitration for a complete removal of aromatics after extraction. Extraction of aromatics from narrow fractions with solvents produced "raffinates" which usually contained about 2 per cent aromatics. These had to be completely removed by various methods, including nitration.

Reaction of Unsaturates with Sulfur Monochloride

A selective and quantitative removal of unsaturates can be performed by certain reagents which, under specific conditions, do not attack other classes of hydrocarbons, *i.e.*, aromatics, paraffins, and naphthenes.

The reaction of sulfur monochloride with low molecular weight olefins was studied by Niemann,¹⁰⁴ Guthrie,⁴¹ Pope and Smith,¹¹⁰ and others. High-boiling sulfochlorinated derivatives, chlorinated sulfides and disul-

fides, are formed as a result of this reaction, such as $(\text{CH}_3 \cdot \text{CHCl} \cdot \text{CH}_2)_2\text{S}$ from propene. Lorand⁸⁰ and Faragher, Morrell and Levine⁸⁰ developed a method using sulfur monochloride for quantitative removal of unsaturates from gasolines: 100 cc of gasoline are treated with 30 cc of sulfur monochloride, added drop by drop. The mixture is allowed to stand over night. Then the solution is cooled by addition of ice and washed two or three times with a 10 per cent solution of alkali and finally with water. The treated gasoline is dried with calcium chloride and filtered. Then it is distilled to 120-125°C at atmospheric pressure, cooled to 30°C, and further distilled in a vacuum to remove the high-boiling compound formed by the action of sulfur monochloride upon unsaturates. The olefin-free distillates obtained are washed with alkali and dried. They contain less than 1 per cent olefins.

Faragher *et al.* determine the percentage of aromatics in the olefin-free gasoline and the total amount of aromatics and olefins by the method described in the previous section. The percentage of olefins is calculated by difference. The figures for the content of olefins and unsaturates produced by this method are very close to those obtained by other reliable methods. Holde⁸¹ in his criticism of this method recommends distilling the unreacted gasoline with steam after treatment with sulfur monochloride to avoid the filtration accompanied by mechanical losses of gasoline to the sulfur produced in the treatment.

Reaction of Hydrocarbons with Halogens

Halogenation of hydrocarbons is a general reaction which yields various mono- and polyhalogenated compounds. Chlorine and particularly bromine are used as halogenating agents. The use of bromine is preferable due to its milder action and better control of the process as compared with chlorination or fluorination. Iodine does not react at all with saturated hydrocarbons, and only very slowly with unsaturates.

The reaction of chlorine or bromine with paraffins, naphthenes and aromatics is very complicated. The substitution of hydrogen atoms by halogen atoms occurs in various places, resulting in the formation of various isomers. In addition to monohalogenated derivatives, di- and polyhalogenated derivatives are formed. Aromatic hydrocarbons may form not only substitution but also addition compounds. The control of all these reactions is frequently impossible. In some cases, however, aromatics form on bromination crystalline substituted tribromoderivatives which may be recrystallized and identified.

Sulfuryl chloride is also a very active chlorinating agent under certain conditions. Kharasch and Brown^{82, 18a} showed that paraffins, naphthenes and side chains of aromatic hydrocarbons are easily chlorinated by this reagent in the presence of minute amounts of peroxides in the dark. Under different conditions, the same reagent produces the sulfonating effect. The reaction of chlorination under the above conditions may be almost quantitative, producing mono- and polychlorinated compounds. Chlori-

nation in the aromatic nucleus does not proceed to any appreciable extent; it is feasible, however, with other catalysts. The reaction is too general to be applied to separation of various classes of hydrocarbons.

Unsaturates may react with bromine selectively at low temperatures so that aromatics, paraffins and naphthenes are not attacked by bromine. The method in question has been developed by Tilicheyev and Massine.¹⁴⁴

According to these authors, the reaction between bromine and unsaturates of cracked gasolines takes place quantitatively at low temperatures of about -20°C , while, under these conditions, aromatics and other hydrocarbons are not attacked by bromine. The dibromides formed are separated by distillation. The method is applied to the narrow fractions of gasolines.

The cracked gasoline under investigation was distilled with a fractionating column into the following fractions: below 60°C , $60-95^{\circ}\text{C}$, $95-122^{\circ}\text{C}$, $122-150^{\circ}\text{C}$, $150-200^{\circ}\text{C}$ and the residue boiling about 200°C .

To determine the approximate chemical composition of the cracked gasoline, the iodine number is determined first by the Hübl-Waller method for each fraction separately (except the fraction boiling below 60°C) and the approximate total content of aromatics and unsaturates is determined by the Kattwinkel method.

The approximate amount of unsaturates present in the given fraction is calculated by the iodine number. The difference between the total of aromatics and unsaturates determined by the Kattwinkel method and the amount of unsaturates gives the approximate content in aromatics. These preliminary tests are indispensable for the analysis to follow.

For the purpose of determining aromatic hydrocarbons (the method is described later) it is essential that the content of unsaturates be not over 20 per cent and that of aromatics not over 7 per cent. If more unsaturates and aromatics are present, the fraction is diluted with an equal, double or triple amount of the fractions which were previously freed from aromatics and unsaturates. These fractions should have approximately the same final boiling points as the fractions under test. The dilution with the gasoline should be such as to give a mixture containing no more aromatics and unsaturates than specified above.

The total of aromatics and unsaturates present in each of the above fractions is then determined by a more accurate method. One hundred and fifty cc of 98-per cent sulfuric acid is admitted into a separating funnel provided with a tight stopper and the whole is weighed to within 0.1 gram. Fifty cc of the fraction under test is then carefully added to the sulfuric acid, by letting the gasoline run down the walls of the funnel. The funnel containing the mixture is then weighed again. This is the manner in which the amount of the fraction used in the investigation is determined. The funnel containing the mixture is placed for 15 minutes in a mixture of ice and water and then carefully shaken in the container with ice. As soon as no more heat is generated, the funnel is removed from the ice container and the mixture is shaken energetically for 30

minutes. After agitation the funnel is weighed again. Losses due to evaporation should not exceed 0.1 gram. The reaction mixture is then allowed to stand over night. The sulfuric acid used is carefully drawn off the next morning. The fraction is discharged through the upper part of the funnel and without any further treatment first into a beaker with a ground stopper, to allow the last drops of the sulfuric acid to settle; after this operation the fraction is finally discharged into a weighed round bottom 50-cc flask. The flask with the fraction is weighed again, thus determining the weight of the fraction left after the sulfuric acid treatment. The product is then distilled with a proper fractionating column. In this operation the temperature observed in the vapors is usually 2 to 40°C higher than the actual final distilling point of the fraction, *i.e.*, corresponding to 95°C, 122°C, etc. The more completely the product was settled and the more complete its separation from the sulfuric acid the smaller is the decomposition, and the smaller is the darkening of the residue left after distillation. The residue left in the flask after the distillation is weighed.

Corrections necessary for losses due to adherence of the fraction to the walls of the container, and to evaporation while transferring from the funnel to the beaker and to the flask are determined experimentally, check experiments being made for this purpose (without distillation) with fractions of corresponding boiling points. The experiments in question required a correction of about 1.5 grams. As has been stated above, the total amount of aromatics and unsaturates equals the loss after the treatment with sulfuric acid and the residue after redistillation.

Since aromatic hydrocarbons are practically absent in the fraction boiling below 60°C, the total of aromatics and unsaturates found in this fraction is accepted as the amount of unsaturates, this being the only determination of unsaturates made for this fraction.

In the remaining fractions the aromatics are determined as follows: forty grams of the fraction under test is charged into a long-neck 200-cc round bottom flask. The weight is determined within 0.1 gram. The flask is then closed with a rubber stopper provided with a thermometer (the bulb is immersed in the liquid) and a glass tube or a small funnel for the admission of bromine.

The flask containing the fraction is placed in a cooling medium of ice and salt. As soon as the temperature of the fraction reaches -20°C bromine is added drop-wise from a burette, the liquid being continuously agitated, and attention is paid to the temperature, which should not exceed -18°C. The theoretical amount of bromine required for the saturation of the unsaturates is calculated by the iodine number.

The bromination is finished when the contents of the flask acquire a bright orange color which does not disappear because of the excess of bromine. This is observed, as a rule, when a few per cent in excess of the theoretically required amount of bromine has been added. The flask containing the reaction mixture is kept in the cooling medium for another

minute. Then 20 cc of a 10-per cent solution of caustic soda is added for the neutralization of the excess bromine. The mixture is agitated and transferred to a separating funnel. The caustic is discharged and the remaining product is washed with water until a neutral reaction is obtained. To obtain a separation of the saturated part of the fraction from the dibromides the product is vacuum distilled. The end of the distillation is indicated by a sharp rise in temperature. The condenser and the receiver must be cooled. This is particularly true for the 60-95°C fraction. The temperature should be kept at about -60°C (solid carbonic acid and alcohol).

Because a part of the dibromides is carried over into the distillate in vacuum distillation, the distillate is redistilled. Two distillations with a dephlegmator are carried out, as a rule, under normal pressure, the second distillation being carried out preferably over metallic sodium.

The original fraction is freed from unsaturates by this method. The determination of aromatic hydrocarbons is then made by the usual aniline method described in Chapter 2.

The method of bromination can be applied only to gasolines and possibly to kerosenes (with certain modifications). For high-boiling fractions, separation of the dibromides formed is practically impossible because of the high temperatures of distillation under which the brominated compounds formed would be decomposed.

The dibromides produced by bromination of olefins can be regenerated to olefins by reaction with copper-zinc couple, zinc dust, etc. This regeneration, however, is not quantitative and is accompanied by some side reactions and formation of tar. Brame and Hunter¹¹ found that the original amylene (trimethylethene) was recovered from the bromide by reaction with copper-zinc couple in neutral alcohol solution in a yield of 40 per cent. Fairly high yields of olefins were obtained by the same workers as a result of regeneration of the bromides formed from narrow fractions of cracked gasolines.

Diolefins form with bromine tetrabromo derivatives. The reaction, however, is not selective, since monoolefins also react with bromine to give dibromo derivatives. The separation of certain diolefins by this method is possible only for some narrow fractions in which a diolefin predominates. Dibromo derivatives have much lower boiling points than tetrabromo derivatives, and are separated by distillation. Brame and Hunter,¹¹ for instance, brominated a 42-47°C fraction of a cracked gasoline containing piperylene (bp 44-45°C), and obtained tetrabromopiperylene, mp 115°C.

Bromine and Iodine Numbers

There is an enormous literature on the method of determining the iodine or bromine number, which can be only partially discussed in this volume. The iodine number tells how much iodine (in per cent by weight) is added under certain conditions to 100 grams of the compound

to be tested. Theoretically, it may be assumed that iodine will saturate all unsaturated valencies of the compound. In this case the iodine number is an exact measure of the unsaturated hydrocarbons (or compounds) present in the product. In practice, the reaction is much more complicated. It may be accompanied by some substitution reactions (particularly with certain branched olefins, naphthenes and aromatics) which increase the iodine number to an extent depending on the concentration of halogen used, time of reaction, and temperature. On the other hand diolefins are usually only partially saturated by iodine or bromine, so that the iodine numbers of these hydrocarbons are much less than would be expected.

If the iodine numbers determine rather accurately the unsaturation of oil products, the percentage of unsaturates can be calculated on the basis of the average molecular weight of unsaturates present in the oil product. For narrow fractions the molecular weight of unsaturates is assumed to be equal to that of the fraction. It is also assumed that each mole of unsaturates is combined with one mole of iodine or bromine. This assumption is true, since monoolefins and other unsaturates with one double bond predominate in petroleum products. Moreover, even diolefins usually combine only with one mole of iodine or bromine under the conditions of determining iodine numbers. Thus the theoretical iodine number of an unsaturated hydrocarbon of the molecular weight, M , is calculated:

$$I = \frac{100 \times 256}{M}.$$

If the theoretical iodine number of a compound or fraction is I and the actual is X , the percentage of an unsaturate or unsaturates in the product is calculated by the formula:

$$P = \frac{100 \times X}{I} \text{ by weight.}$$

The calculation of the percentage of unsaturates on the basis of iodine numbers is possible only for low-boiling fractions, *e.g.*, for gasolines and kerosenes. It should be emphasized that the agreement between the theoretical iodine numbers and those determined by the methods to be discussed was proved only for low-boiling unsaturated hydrocarbons. For high-boiling fractions, *e.g.*, lubricating oils, the iodine numbers have only relative value, and should be considered as only approximate indices of unsaturation.

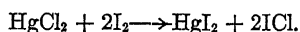
Iodine as such is not used extensively for determining iodine numbers, as the reaction between iodine and unsaturated hydrocarbons is too slow. Iodine, however, can be used in alcohol or acetone solutions, in which it reacts more rapidly with unsaturated hydrocarbons. Chlorine is not used for the opposite reason: it is too reactive and produces many substitution reactions. Thus iodine chloride, iodine bromide, and bromine and iodine in solutions of alcohol, acetone, acetic acid, chloroform or

carbon tetrachloride are employed for determining the unsaturation of oil products in various modifications to be discussed in this section. The nature of the solvent may affect the result to a certain degree. There are indications that the use of carbon tetrachloride is objectionable in view of the interaction with hydrocarbons in the light. Rhodan radical SCN can also be used for the saturation of unsaturated valencies, as well as some organic peroxides which form compounds with the double bonds of unsaturated hydrocarbons. The results obtained with bromine, rhodan, etc. are frequently recalculated for iodine.

The concentration of the reagent, reaction time, and temperature must be kept within limits in which substitution reactions are practically eliminated. The determination is carried out at room temperature and in darkness.

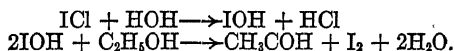
The methods of determining iodine and similar numbers can be summarized as follows:

(1) Von Hübl's method uses ICl in alcohol solution: 25 gr of I_2 are dissolved in 500 cc of 95 per cent ethyl alcohol; 30 gr of $HgCl_2$ are also dissolved in 500 cc of the same solvent. Both solutions in equal volumes are mixed at least two days before use to give the reaction forming ICl:



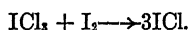
Usually 25 cc of the final mixture are employed for the determination. The weight of the product to be tested depends upon the unsaturation, and should be sufficient to consume about $\frac{1}{3}$ of the halogen. This applies to all methods described below. The weighed amount of the product is dissolved in 10 cc of chloroform or carbon tetrachloride. The reaction time is about 24 hours. When the reaction is completed, 20 cc of 10 per cent potassium iodide solution and 130 cc of water are added, and iodine formed is titrated with 0.1 N $Na_2S_2O_3$ solution.

(2) Waller's modification of the Hübl method. Strong hydrochloric acid is added to the Hübl solution to suppress the hydrolysis of ICl and oxidation:



As a result, Waller's reagent is more stable than Hübl's.

(3) Wijs' method uses ICl in glacial acetic acid to avoid completely the reactions of hydrolysis and oxidation given above: 7.5 gr of ICl_3 and 8.2 gr of I_2 are dissolved in glacial acetic acid to make one liter of solution. As a result, ICl is formed:



The weighed amount of the product is dissolved in 10 cc of chloroform or carbon tetrachloride, and 25 cc of the ICl solution are added. The reaction time is from one to two hours. After the reaction is completed, 15 cc of 10 per cent KI solution and 100 cc of water are added. The titration is carried out as described for Method 1.

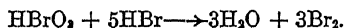
(4) Hanus' method uses iodine bromide in glacial acetic acid: 10 gr of IBr are dissolved in 500 cc of glacial acetic acid, and 25 cc of this solution are employed for the reaction. A weighed amount of the product is dissolved in 10 cc of chloroform. The reaction time is 30 minutes. When the reaction is completed, 15 cc of 10 per cent KI solution and 50 cc of water are added. The titration is as in Method 1. A modification of this method has been used and described by Dean and Hill.²⁰

(5) Kaufmann's method uses bromine in methyl alcohol: 5.2 gr of bromine are dissolved in 1 liter of a saturated solution of NaBr in methyl alcohol; 25 cc of this solution are added to the weighed amount of the product in 10 cc of chloroform. The reaction time is 3 hours. When the reaction is completed, 15 cc of 10 per cent KI solution are added, and the titration proceeds as in Method 1.

(6) Uhrig and Levin¹⁴⁹ modified Method 5 by direct titration with bromine in glacial acetic acid (2 per cent solution). A weighed amount of the product, from 0.1 to 1.0 gr, is dissolved in 5 cc of chloroform and titrated directly (no indicator) with the bromine solution until a distinct orange-yellow color is obtained, which persists for about 15 seconds.

(7) Margosches' method uses iodine in alcohol: 25.4 gr of iodine are dissolved in 1 liter of 90 per cent ethyl alcohol; 20 cc of the solution are mixed with the weighed amount of the product dissolved in 10 cc of absolute alcohol; 200 cc of water are added, and the mixture is shaken for 3-5 minutes. The excess of iodine is titrated with 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ (no KI solution is added).

(8) Winkler's method: bromine is produced in water solution from KBrO_3 and KBr in the presence of an acid:



A 0.1 N solution of KBrO_3 is prepared, 50 cc of which are added to the weighed amount of the product in 10 cc of carbon tetrachloride. To the mixture are added: 1 gr of KBr and 10 cc of 12.5 per cent hydrochloric acid. The time of reaction is about 2 hours. When the reaction is completed, 15 cc of 10 per cent KI are added. Titration is as in Method 1.

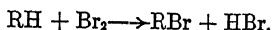
(9) Francis' method is a modification of Method 8: 14 gr of KBrO_3 and 50 gr of KBr are dissolved in water to form 1 liter of solution. The weighed amount of the product without any solvent is mixed with a suitable volume of the above solution, to which 5 cc of H_2SO_4 are added. The mixture is shaken vigorously for a minute. Then 15 cc more of acid are added to complete the liberation of bromine, and the shaking is continued for another minute. If the solution is colorless, a little more bromide-bromate solution is added, and so on until the final color turns light yellow. One or two cc of saturated KI solution are added, and the iodine liberated is titrated as usual.

To keep the excess of potassium bromate-bromide to a definite minimum, Lewis and Bradstreet⁷⁵ modified the Francis procedure as follows: 20 cc of 10 per cent H_2SO_4 saturated with KBr and 15 cc of *n*-heptane or

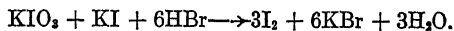
other suitable solvent are mixed with the weighed amount of the product (from 0.7 to 1.0 gr). Then follows a direct titration with 0.5 *N* KBr-KBrO₃ to a faint yellow color. An excess of 1 cc of this solution is added, and the mixture is shaken for 2 minutes. Finally, 5 cc of saturated KI solution are added, and the iodine is titrated as usual.

(10) Rosenmund and Kuhn¹¹⁶ suggested the determination of bromine numbers in the presence of pyridine or quinoline. These compounds or their salts react readily with bromine to form dibromide addition compounds, which are mild bromination agents and readily brominate unsaturated hydrocarbons. The procedure is as follows: a weighed amount of the product is mixed with glacial acetic acid and pyridine or quinoline in the form of a HCl-salt. A bromine solution is used for titration. As soon as the product has been brominated, the formation of dibromide addition compounds can be noted by an orange-yellow color. The method is not used to any large extent. Hammerich⁴² found a very close agreement between theoretical bromine numbers and those determined by this method.

(11) McIlhiney's method differs substantially from the other methods described. Bromine is used for a prolonged time, resulting in a complete addition of bromine to unsaturated hydrocarbons and in a considerable effect of substitution reactions:



The HBr formed is determined quantitatively to segregate the substitution effect from the addition effect. A weighed amount of the product in 10 cc of carbon tetrachloride is mixed with 20 cc of 0.33*N* bromine solution in carbon tetrachloride. The reaction time is from 30 minutes to several hours. When the reaction has been completed, 20 to 30 cc of 10 per cent KI solution and 75 cc of water are added, and the iodine liberated is titrated as usual. In this way the total iodine or bromine number is determined. The hydrobromic acid formed as a result of the substitution is determined by reaction with KIO₃ and the iodine formed is determined by titration:



The addition iodine number is calculated by subtraction of the substitution iodine number from the total.

(12) Kaufmann's and Grosse-Oetringhaus' method⁸⁴ uses iodine rhodanate in carbon tetrachloride: 25 cc of 0.2*N* solution of iodine rhodanate in carbon tetrachloride are mixed with the weighed amount of the product in 10 cc of carbon tetrachloride. The reaction time is 18 hours. When the reaction is complete, 50 cc of 10 per cent KI solution are added (an excess is necessary to suppress the hydrolysis of unreacted ISCN. The iodine is determined by titration.

It should be clearly emphasized that almost any of the methods de-

scribed can be used for determining the unsaturation of petroleum products under specific conditions with more or less satisfactory results. On the other hand, none of the methods may be considered as universal and satisfactory for all products under the same conditions. The main condition is the time of reaction. Theoretically, the bromine or iodine number should be independent of the reaction time, *i.e.*, the iodine number should not change with time after complete saturation of the unsaturates. In practice, the iodine number frequently increases gradually, mainly because of substitution reactions. In such cases, either the modification of the method is unsatisfactory for the product investigated, or the optimum reaction time for completing the addition reactions should be found experimentally. The second important factor is the concentration or excess of halogen. As in the previous case, an excess theoretically cannot affect the iodine number, but in practice it does so on account of substitution reactions. The relative amounts of halogen used in the above modifications of the method should be considered as those which, on the average, insure completion of the addition reactions and do not favor substitution reactions.

The McIlhiney method differs basically from the others in that it determines the effect of substitution. This idea is entirely sound, but from a practical standpoint the method adds the difficulties of determining the substitution number to those of determining the addition number. For instance, the brominated product can split off hydrogen bromide in a later stage of the determination, thus increasing the substitution number and correspondingly decreasing the addition number. As a result, the addition numbers obtained by this method are difficult to reproduce and are sometimes negative. However, deKok, Waterman and van Westen⁷⁰ obtained good results for individual normal olefins and cycloolefins by this method. Apparently, it can be applied only to products containing low molecular weight olefins, which produce stable brominated compounds. For cracked gasolines, as well as for other products, the iodine numbers obtained by this method are unreliable and usually much lower than those found by other methods. Tannich *et al.*¹³⁸ obtained in many cases satisfactory agreement between the results produced by the McIlhiney and the iodine-rhodanate methods for various fractions of a cracked naphtha; but in general the unsaturation determined by the McIlhiney method was substantially lower than that indicated by the iodine-rhodanate method. On the contrary, for high-boiling fractions and products the McIlhiney method apparently gives more reliable results than other methods do. It should be mentioned that hydrocarbons of the naphthalene or tricyclic aromatic structure react readily with bromine and thus give high bromine numbers. The reaction, however, is due to the substitution and is accompanied by formation of hydrogen bromide. Application of the McIlhiney method to these hydrocarbons usually gives a satisfactory separation of substitution and addition effects, so that the addition bromine numbers deter-

mined by this method are close to zero, indicating the aromatic character of such hydrocarbons and absence of active double bonds.

The Hübl or Hübl-Waller methods (1 and 2) may give fairly reliable results for petroleum products. The Hübl iodine number is usually almost independent of the reaction time, and the substitution reactions are therefore almost eliminated. However, the Hübl iodine numbers are usually somewhat lower (about 10 per cent) than those of the other methods discussed. It is believed that the Hübl method gives a somewhat lower percentage of unsaturation than the actual. The instability of the Hübl reagent limits the application of this method and its modifications for petroleum products.

The data on the methods of Margosches and Winkler are very meager. The Winkler reagent, bromine in water solution, may have a strong effect on the substitution reactions. Margosches, Krackowetz and Schnabel¹⁸⁶ showed that the Margosches method gives results very close to those of the Hübl method. Other workers, however, found that the iodine numbers by the Margosches method are low, compared with those of other methods. In view of this controversy, the method so far cannot be recommended.

The methods of Hanus, Wijs and Kaufmann usually give very close results for gasolines or individual low molecular weight hydrocarbons. As stated above, the Hanus, Wijs and Kaufmann iodine numbers are somewhat higher (about 10 per cent) than the Hübl numbers. The disadvantage of these methods is a steady increase of the iodine number with reaction time caused by the substitution reactions. Thus the reaction time should be specified and experimentally determined for any specific material. The values of the reaction time given above are only averages. Faragher, Gruse and Garner,²⁹ Tropsch and Koch,¹⁴⁷ and others found good agreement between the theoretical iodine numbers and those obtained by the Hanus and Wijs methods for various hydrocarbons. Koch and Hilderath⁶⁹ thoroughly tested these methods by comparing them with theoretical values, and determined iodine numbers experimentally for various hydrocarbons. Normal, slightly branched and cyclic olefins give results which are almost identical with the theoretical figures. Highly branched olefins, such as 3,4-diethylhexane-2 or diisobutene, give much too high iodine numbers (as compared with theoretical) because of substitution reactions. On the contrary, diolefins, such as isoprene or cyclopentadiene, not being completely saturated by halogen under the conditions of the methods, give iodine numbers about one-half of theoretical. The same result was obtained by Faragher *et al.*

The application of the Hanus, Kaufmann and Wijs methods to high-boiling fractions and products gives less reliable results. Substitution reactions occur readily with such fractions, resulting in a steady increase in the iodine number with time (Hanus and Wijs). The addition and substitution reactions take place simultaneously, and the iodine numbers determined by these methods relate to the complex of addition and sub-

stitution processes. The Kaufmann method gives more reliable results because of the specific properties of the reagent used. As stated above, the Kaufmann reagent is 0.2*N* solution of bromine in methyl alcohol saturated with sodium bromide. Bromine, on combining with sodium bromide, probably forms a complex, NaBr_3 , which is a much milder brominating agent than the free halogens used in the other two methods. The iodine numbers of heavy oils determined by the Kaufmann method increase with time slowly and are more or less close to those determined by the Hübl method. The Hanus and Wijs methods invariably give iodine numbers which may be twice as high as the Hübl or Kaufmann numbers. The iodine numbers for heavy oils have only a relative character, and cannot be used for approximate calculation of the percentage of unsaturated hydrocarbons.

The results obtained by Uhrig-Levin's method seem to be as good as or better than those of Kaufmann's. In the former, bromine solution is used directly and, as a result, no excess bromine is employed. The iodine numbers of diisobutene and triisobutene determined by this method are very close to the theoretical values.

It is believed that the Hanus, Wijs and Kaufmann methods give satisfactory results for the unsaturation of cracked gasolines or low-boiling gas oils. Highly branched olefins and diolefins, which give erratic results, are represented in these products, usually in a small proportion.

Francis' method³⁴ is widely used in the United States. As has been pointed out by the author, bromine is generated slowly during the determination by making the solution only slightly acidic. As a result, the bromine concentration is kept low, and substitution reactions are avoided. Cortese¹⁷ and Mulliken and Wakeman⁹⁶ determined bromine numbers of a series of hydrocarbons by the Francis method. The agreement between theoretical values and those found by this method was satisfactory for olefins (including branched), cycloolefins, and diolefins. Only for some diolefins was the saturation incomplete and the bromine numbers appreciably smaller than theoretical. The saturation of some anthracene derivatives was incomplete, and terpenes gave erratic results. In view of the absence of such hydrocarbons in petroleum oils, the erratic results obtained on these hydrocarbons seem to be unimportant. Lewis and Bradstreet⁷⁵, however, found that the Francis method also gives high figures for highly branched olefins, and suggested another modification of this method, described above, which is claimed to give better results because of the minimum excess of bromine. Green³⁷ also found that the Lewis-Bradstreet modification gives more consistent results than the original method.

The Francis method has the advantage of simplicity. There are no comparative data on the unsaturation determined by this and by other reliable methods for high-boiling fractions. It is surprising that this trustworthy and convenient method (at least for gasolines and low-boiling fractions) has found no application in Europe.

Kaufmann and Grosse-Oetringhaus⁶⁴ developed a new method for determining unsaturation by the use of iodine rhodanate. Its advantage is the absence of substitution reactions, which is due to the mild halogenating properties of this reagent. In this respect, this method is preferable to all the others discussed. Koch and Hilderath⁶⁸ showed that it gives almost theoretical iodine numbers for all olefins, including highly branched hydrocarbons such as 3, 4-diethylhexene-3, for which other methods invariably give high iodine numbers caused by substitution reactions. As might be expected, the iodine number of diolefins determined by this method is only one-half of the theoretical. According to Grosse-Oetringhaus, the iodine numbers of heavy petroleum oils determined by the iodine-rhodanate method are pretty close to the values obtained by the Hübl and Kaufmann methods.

In addition to halogens, such reagents as perbenzoic acid or other peracids can be used for determining unsaturation. Perbenzoic acid reacts with unsaturates at 0°C, forming olefin oxides which are hydrolyzed to glycols. The method developed by Nametkin and his associates^{101, 102} is carried out as follows. A weighed quantity of perbenzoic acid is reacted with a weighed amount of the oil for two days. Then the unreacted perbenzoic acid is decomposed with an excess of a KI solution. The liberated iodine is titrated with sodium thiosulfate. In this way the perbenzoic number, *i.e.*, the amount of the acid required for the reaction with 100 gr of the oil, is determined. The method is similar to the determination of iodine or bromine numbers and gives results which are rather close to those produced by the last methods described for gasolines. For high-boiling fractions, particularly lubricating oils, the values of unsaturation obtained by this method are much higher than those calculated from iodine numbers, because of the reaction of other hydrocarbons with perbenzoic acid.

Separation of Unsaturates and Aromatics with Mercurial Salts

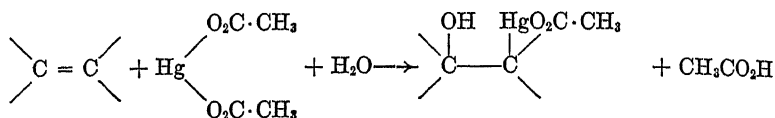
Deniges was the first to observe the formation of compounds of mercuric salts with olefinic hydrocarbons.²² These compounds, acidified with strong acids, recover the original olefins. Tausz¹³⁹ used mercuric acetate in water or alcohol solutions for this reaction. Many olefins form compounds with mercuric acetate only in alcohol solution; such compounds are readily decomposed in aqueous solutions. Hugel and Hibou⁵⁵ obtained a series of mercuric compounds with various olefins, including hexadecene, in glacial acetic acid.

Some branched olefins are oxidized by mercuric acetate so that formation of the complex compounds is not a single reaction between the mercuric salt and olefins. For instance, Balbiano and Paolini⁵ oxidized trimethylethene with mercuric acetate into acetaldehyde and acetone.

Cyclic olefins and diolefins react with mercuric salts in the same manner as olefins.

Hofmann and Sand⁵⁰ and later Sandborn and Marvel¹²⁵ showed that

the organic mercurial compounds are not molecular addition products but correspond to the general formula:



If methyl alcohol is used instead of water, the CH_3O group replaces the hydroxyl group.

Riesenfeld and Bandte¹¹² found that olefins may be quantitatively removed only by an excess of mercuric acetate. For instance, amylene from 10 per cent solution was completely removed by the treatment of 50 cc of the solution with 60 gr of mercuric acetate for 8 hours. The reaction of olefins with mercuric acetate is slow and frequently requires repeated treatments. For instance, Morgan and Soule⁹⁴ found this to be true for the 173-237°C fraction of a low-temperature tar.

Brame and Hunter¹¹ and Tropsch and Koch¹⁴⁷ showed that organic mercuric compounds, both in aqueous and methyl alcohol solutions, absorb an appreciable quantity of saturated hydrocarbons. Thus the regeneration of olefins from mercuric compounds produces olefins which are contaminated with saturated hydrocarbons. These authors recommended stripping the organic mercuric compounds either by steam or in a vacuum. Mercuric compounds treated in this way give pure olefins on regeneration.

The procedure is as follows: 50 gr of mercuric acetate are mixed with 150 cc of methyl alcohol, the dissolution of the salt being incomplete. A weighed amount (*e.g.*, 100 gr) of a petroleum product is added to the above mixture; it is taken in an excess with respect to the unsaturates present. The reaction mixture is shaken for an hour at room temperature. The acetic acid formed is neutralized by normal (or stronger) potassium hydroxide solution. The complex mercury compound formed is further reacted with a strong solution of potassium bromide taken in an amount sufficient to convert the total quantity of mercuric acetate used. The new complex mercury compound formed is now separated as a heavy, yellow, oily liquid. The upper water-alcohol solution is removed. The yellow liquid is filtered and heated on a steam bath in a vacuum to remove by distillation the absorbed saturated hydrocarbons, as described above. It is recommended to add a small amount of methyl alcohol after distillation and to redistill this and the traces of saturated hydrocarbons.

The complex compound is then decomposed by 10-15 per cent hydrochloric acid at room temperature. The unsaturated hydrocarbons formed are washed with water until a neutral reaction is obtained. The use of alkaline solution is not recommended in view of the formation of emulsions. The unsaturates recovered by this method are practically pure. Tropsch and Koch¹⁴⁷ separated almost pure olefins from fractions of a synthetic gasoline (Fischer-Tropsch process) by this method, and Tili-

cheyev and Massine¹⁴⁵ from fractions of a cracked gasoline. The purity of the olefins separated by Tropsch and Koch was checked by comparison with individual olefins. Tilicheyev and Massine separated narrow fractions of olefins having an iodine number close to the average theoretical value for olefins boiling in the range of the fractions.

According to Brame and Hunter, however, only a part of the unsaturated hydrocarbons is removed by mercuric salts. Oxidation of some iso-olefins should also be kept in mind. The recovery of olefins from complex mercuric compounds is only partial, since some secondary reactions destroy another part of the unsaturates. Tilicheyev and Massine confirmed the results of Brame and Hunter. They found that only about 50 per cent of the olefins present in cracked fractions were removed by the reaction with mercuric acetate, where as the other 50 per cent remain unreacted in the fractions. In addition to this, only 25 per cent of the original olefins were recovered from mercuric complex compounds.

It should be borne in mind that aromatic hydrocarbons also may react with mercuric salts,^{68, 159} particularly mercuric acetate, forming mercurates:



The reaction, however, is much slower than with olefins and takes place at temperatures from 90 to 160°C under pressure for two or three hours. Thus the reaction with aromatics will not interfere with the reaction with unsaturates under the mild conditions specified for the removal of the latter.

The mercurial method in its present modification can be applied only to cracked gasolines and other low-boiling fractions. For high-boiling fractions, the mercuric compounds formed absorb a considerable proportion of unreacted material which cannot be separated by distillation, as is the case for cracked gasolines. In addition, the high molecular weight olefins react with mercuric salts slowly and only partially. The method in question can successfully be used for identification of some olefins present in cracked gasolines, but not for quantitative separation. Advantages of the method are its selectivity and the easy regeneration of original unsaturates.

The treatment of straight-run products with mercuric acetate may be used for incomplete separation of aromatics. Toluene and other derivatives of benzene react with mercuric acetate with ease, and produce mercurial compounds by refluxing. Naphthalene and its derivatives are also mercurated. Besides mercurial salts, some salts of other heavy metals, particularly silver nitrate, may be used for separation of low molecular weight olefins.

Hydrogenation of Unsaturates

Hydrogenation of fractions is one of the new and effective methods of investigating the chemical composition of petroleum. Two principal

types of compounds are involved in the process, namely, unsaturates, chiefly olefins, and aromatics.

It is well known that unsaturates are hydrogenated much more easily than aromatics. Hydrogenation of unsaturates may be carried out selectively at low pressures and/or low temperatures. Under these conditions the most active hydrogenation catalysts are used, *i.e.*, platinum, palladium, or nickel.

Waterman, Perquin and van Westen¹⁵⁴ used a palladium catalyst and completely hydrogenated pentene at room temperature and atmospheric pressure, whereas benzene under these conditions was not hydrogenated at all. Ipatieff and Corson⁵⁷ hydrogenated a mixture of olefins and aromatics in the presence of a nickel catalyst on kieselguhr at 20-50°C and high hydrogen pressure (100 kg per sq inch initial), or at 115-175°C and atmospheric pressure of hydrogen. In both operations only olefins were selectively hydrogenated.

DeKok, Waterman and van Westen⁷⁰ selectively hydrogenated unsaturates at 220°C and atmospheric pressure in the presence of palladium on activated carbon; palladium chloride was blended with activated carbon and reduced by hydrazine hydrate in alkaline solution. Olefins, diolefins and cycloolefins were completely hydrogenated, whereas styrene was hydrogenated into ethylbenzene. It is of interest that the hydrogenation of styrene under the same conditions but in the presence of a platinum catalyst produced ethylcyclohexane. The authors draw attention to the fact that hydrogen completely saturates diolefins, whereas halogenation (in determining iodine numbers) frequently gives only a partial effect of saturation with these hydrocarbons.

Under mild conditions hydrogenation can be used for investigating the chemical structure of olefins, since it usually does not affect the general structure of hydrocarbons, *i.e.*, the number and the position of side chains. For instance, Hoog, Smittenberg and Visser⁵⁴ hydrogenated the polymer of isobutene obtained as a result of polymerization with a phosphoric acid catalyst. Fractionation of the hydrogenation product showed that it consisted largely of 2,2,4-trimethylpentane (70 per cent) and of 2,3,4-trimethylpentane (15-20 per cent). Thus the original polymer consists mainly of two olefins of the same structure.

Even in the presence of molybdenum catalyst the hydrogenation of unsaturates may be selective, if comparatively moderate temperature conditions are employed. Vlughter¹⁵¹ hydrogenated cracked distillates at 300°C and 100 atmospheres' initial hydrogen pressure, and showed that only olefins were hydrogenated under these conditions, aromatics being unchanged. This finding is of importance, as the process is carried out in the presence of a sulfur-resistant catalyst. Otherwise, in the presence of such catalysts as platinum or nickel, the hydrogenation of unsaturates requires several repeated operations, with fresh catalyst taken in excess.

The procedure for hydrogenating cracked product for the selective removal of unsaturates is as follows: 200 cc of cracked gasoline and 40 gr

of a molybdenum catalyst are charged into a rotating hydrogenation autoclave with a capacity of 2 liters. Hydrogen is pumped in until the pressure reaches about 100 atmospheres. Then the autoclave is heated to 300°C. At this temperature it is kept until the pressure, which at first decreases due to the hydrogenation, has remained constant for 30 minutes. Then the heating is stopped and the apparatus is cooled to about 200°C. At this temperature the hydrogen and the hydrogenated gasoline are passed hot through the valve of the autoclave, and the thoroughly cooled gasoline is collected in a receiver. Thus filtration of the catalyst from the hydrogenated gasoline is unnecessary.

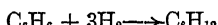
If a high-boiling product or fraction is hydrogenated, separation of the catalyst is performed by filtration, after which the catalyst is thoroughly washed with a low-boiling solvent which is then removed by distillation. In this case the autoclave is cooled to room temperature. The saturation of unsaturates under the above conditions is very complete, and the bromine number after hydrogenation does not exceed 2.

If the cracked gasoline is very unsaturated (*e.g.*, vapor phase-cracked), some side polymerization and condensation reactions may accompany hydrogenation. In such cases hydrogenation is performed in two stages. In the first stage a nickel catalyst (20 gr per 200 cc of gasoline) is employed, with the same pressure as given above, but the temperature does not exceed 150°C. The contents of the autoclave are allowed to escape through the valve. In this operation all unstable and easily polymerizable diolefins and other unsaturates are hydrogenated. In the second stage, the product of the first stage is hydrogenated with a molybdenum catalyst in the same manner as for the one-stage process.

After selective hydrogenation of unsaturates, the content of aromatics may be determined by the sulfuric acid method or any other suitable process. The total amount of unsaturates and aromatics is determined by absorption with sulfuric acid, followed by redistillation to the end point of the original product (page 165).

Hydrogenation of Aromatics

Hydrogenation of aromatics is carried out either with straight-run products, free of unsaturates, or with cracked products after the selective hydrogenation of unsaturates. In the presence of unsaturates, both classes of hydrocarbons will be hydrogenated under the conditions described in this section. The catalytic hydrogenation of aromatics takes place (*e.g.*, for benzene) according to the equation:



The reaction proceeds in one stage without formation of any partially hydrogenated benzenes. Hydrogenation of polycyclic aromatics takes place in consecutive stages, *i.e.*, the rings are hydrogenated in consecutive order. Each ring, however, is hydrogenated completely, as in the case of benzene. In the presence of active catalysts and an excess of hydrogen,

hydrogenation may be complete, *i.e.*, all aromatic rings may be completely saturated.

As has been pointed out, the non-destructive hydrogenation of aromatics present in petroleum fractions and products is a very important operation for evaluating their ring content and structure. The aromatic hydrocarbons are much more resistant to hydrogenation than are unsaturates. Non-destructive hydrogenation of aromatics in the presence of sulfur-resistant catalysts (molybdenum disulfide, etc.) is practically impossible. The aromatic hydrocarbons are affected by hydrogen in the presence of such catalysts at temperatures from about 350 to 400°C. As a result, hydrogenation is frequently accompanied by decomposition reactions, including partial opening and degradation of polyaromatic rings.

Accordingly, more active catalysts, such as nickel or platinum, are used for this purpose of aromatics. Vlугter, Waterman and van Westen¹⁵⁸ recommended hydrogenation at 250-300°C (maximum 350°C), at a starting pressure of 100-120 kg/cm.² The catalyst is finely divided nickel on kieselguhr. In most cases hydrogenation must be repeated many times with fresh catalyst because of the poisoning effect of sulfur compounds in the oil. Hydrogenation is complete when hydrogen is no longer absorbed and the constants (specific gravity, refractive index, etc.) no longer change. The specific dispersion of the totally hydrogenated oil must be not higher than 100/10⁴ (Chapter 2). Müller and Neyman-Pilat⁹⁵ also pointed out the difficulty of hydrogenating completely aromatic hydrocarbons in oils at moderate temperatures, even in the absence of sulfur compounds. They dissolved the oil product in pentane and hydrogenated at 270°C, the initial hydrogen pressure being 120 atmospheres. Nickel on activated earth was used as a catalyst. At this temperature hydrogenation, even of a sulfur-free fraction, required 7 consecutive runs.

Mair, Willingham and Streiff⁸⁴ described a similar procedure. They hydrogenated lubricating-oil fractions containing sulfur and nitrogen compounds. The temperature was from 230 to 250°C, the initial hydrogen pressure above 100 atmospheres, the time from 10 to 12 hours. The number of treatments was from 5 to 10; and the catalyst used was nickel-on-kieselguhr, or Raney's nickel. The fraction to be hydrogenated (12 to 30 gr) was dissolved in methylcyclohexane (75 cc) and was hydrogenated in the presence of from 3 to 50 gr of the above catalyst in each hydrogenation. An excess of catalyst is recommended for fractions high in sulfur. The sulfur was removed completely by using 50 gr of Raney's nickel in the first treatment.

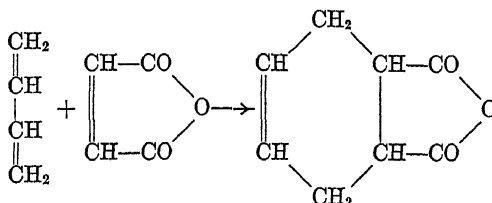
Recently Waterman and van Vlodrop¹⁵⁵ also pointed out that complete hydrogenation of sulfur-containing products may be carried out in a limited number of operations (*e.g.*, three) by using a very large excess of a nickel catalyst (100 per cent or more). The temperature of hydrogenation is 280-290°C, the initial hydrogen pressure 100 atmospheres and

the time one hour. It has been proved that the excessive proportion of catalyst did not involve any undesirable side reaction.

The non-destructive hydrogenation of straight-run heavy, dewaxed fractions is of particular importance. Such fractions consist of aromatics and naphthenes, neglecting a small proportion of oxygen, sulfur and nitrogen compounds. Thus hydrogenation, converting aromatics into naphthenes, produces purely naphthenic fractions which can be further investigated with respect to their ring structure and the content of paraffinic side chains (Waterman *et al.*,¹⁵² Rossini¹¹⁸).

Separation and Identification of Diolefins by Condensation

Diels and Alder²⁵ discovered that conjugated diolefins, cyclic and aliphatic, react with maleic anhydride as follows:



The condensation products are characterized by their perfect crystalline form. Since the melting points of the anhydrides produced from the simplest diolefins differ substantially (with one exception), identification of the original diolefins is comparatively simple by this method (Table 47).

Table 47. Properties of Diolefins and Anhydrides.

Diolefin	Boiling Point (°C)	Melting Point of anhydride (°C)
Butadiene-1,3	-10	103-104
Isoprene	33-35	63-64
Piperylene	42-44	62
Cyclopentadiene	41	164-165
1,3-Cyclohexadiene	81-82	147

The reaction of maleic anhydride with cyclopentadiene and its derivatives is almost instantaneous. The reaction with aliphatic diolefins is much slower and is accompanied by polymerization, which is apparently catalyzed by maleic anhydride.

The procedure described by Birch and Scott⁸ is as follows. The fraction containing diolefins is carefully dried and filtered. It is then cooled in ice, and several grams of finely divided maleic anhydride are added. For identification purposes it is advisable to have an excess of the diolefin. The flask is vigorously shaken to dissolve the anhydride. The following procedure depends upon the diolefin present.

(1) In the presence of cyclopentadiene and its derivatives, crystallization is rapid. The flask must be cooled in ice if the quantity of diole-

fin is fairly large. To insure complete crystallization, the flask with reagents is left overnight. The anhydrides formed by cyclopentadiene derivatives are almost insoluble in cold gasolines and are separated by filtration. They can be recrystallized from petroleum ether.

(2) In the presence of aliphatic diolefins the reaction is slow, and is continued in ice for several days. If the concentration of aliphatic diolefins is very low, the reaction is carried out by heating to 100°C in an autoclave for several hours. The anhydrides formed are crystallized only after evaporation of an excess of gasoline, and are purified by crystallization from benzene or petroleum ether. In some cases the condensation products are contaminated with rubber-like polymers, from which the anhydrides are freed by crystallization.

Kurtz and Headington⁷⁸ use the following procedure for the separation of conjugated diolefins. The sample is stripped by fractionation of all fractions boiling below 40°C. Six hundred cc of the stripped sample are treated with 60 gr of freshly distilled maleic anhydride by heating in a 1-liter flask on a steam bath for one hour. A reflux condenser is maintained at -10°C. Then the sample is cooled, the upper layer decanted from maleic anhydride, and enough 10 per cent sodium hydroxide solution is added to the maleic anhydride in the flask to dissolve it. The resulting solution is added to the hydrocarbon layer in a 1000-cc separatory funnel, and after shaking and settling, is drawn off. One hundred cc of fresh 10 per cent NaOH solution are added to the hydrocarbons in the funnel, shaken, and drawn off. The hydrocarbons free of conjugated diolefins are then washed twice with 100 cc of water. Handling losses are determined in a blank treatment and are of the order of 1 per cent.

Tropsch and Mattox¹⁴⁸ developed a simple method of determining butadiene-1, 3 in gases by absorption by molten maleic anhydride at 100°C. From 2 to 2.5 grams of freshly distilled maleic anhydride are heated to 100°C in a shallow dish and drawn into a special heated absorber. A sample of the gas to be analyzed is passed into the absorber. The volume of the gas is measured after absorption, the difference being due to the butadiene absorbed. The molten maleic anhydride is saturated with the gas before absorption to avoid physical solution of the hydrocarbons in the molten maleic anhydride. Neither olefins nor paraffins react with the anhydride.

Absorption by molten maleic anhydride may also be applied to the determination and quantitative separation of conjugated diolefins in liquid fractions, which are evaporated and reacted with maleic anhydride at 100°C. However, the reaction is complicated with the side reaction of maleic anhydride with tertiary olefins. The addition of 2-3 per cent of a high-boiling primary or tertiary amine is said to prevent or inhibit the latter reaction.

Unfortunately, there are other complications which may limit the wide use of this excellent method. Farmer and Warren³¹ found that certain methylated butadienes are easily polymerized in the presence of

phthalic anhydride. In such cases the condensation must be carried out very slowly at a low temperature in the initial stage; 4-methylpentadiene-1,3 did not react with phthalic anhydride. Recently Robey, Morrell and Wiese¹¹⁴ noticed that the condensation of pentadiene-1,3 with phthalic anhydride is not complete and stops abruptly as soon as most of the pentadiene has condensed. The uncondensed portion corresponds to *cis*-pentadiene-1,3, which does not react with phthalic anhydride.

Reactions of Tertiary Hydrocarbons with Chlorosulfonic and Fuming Sulfuric Acids

It is well known that normal and quaternary paraffins are more resistant to such active reagents as chlorosulfonic or fuming sulfuric acids than are tertiary isoparaffins. Naphthenes containing a tertiary carbon atom are similar to tertiary isoparaffins in reactions with these reagents. Thus, various alkylated derivatives (with the exception of dialkyl derivatives of type 1,1) of cyclohexane or cyclopentane react with the above acids, whereas cyclohexane or cyclopentane themselves are only slightly affected. Hydrocarbons with tertiary carbon atoms are easily attacked by the above-mentioned acids and form various products of oxidation, sulfonation, etc. These reactions can be used for more or less quantitative separation of normal paraffins from isoparaffins or, generally speaking, from all hydrocarbons containing tertiary carbon atoms.

Aschan⁴ was the first to discover that isopentane and diisopropyl react with chlorosulfonic acid and completely dissolve in it. Hydrogen chloride is readily formed. Young¹⁶³ used this method for purification of normal paraffins produced from gasolines.

Shepard and Henne¹³² treated with chlorosulfonic acid the decane fraction separated from a gasoline, vigorously stirring at room temperature. A sample of 1,700 cc was treated with 300 gr chlorosulfonic acid. The reaction was slow. Every 3 or 4 days the spent acid was replaced by fresh acid; about 3 kilograms of the acid were used altogether. Complete removal of the isoparaffins and other hydrocarbons containing tertiary carbon atoms required almost 4 weeks of treatment.

Shepard, Henne and Midgley¹³³ prepared chemically pure normal paraffins, from hexane to dodecane, by treatment of the corresponding fractions produced from a gasoline. Each fraction was treated with chlorosulfonic acid under the conditions specified above. Virobianz *et al.*¹⁵⁰ treated paraffinic gasoline fractions produced from Grozny and Maikop crudes, to remove isoparaffins at elevated temperatures: C₆-fraction at 55°, C₇-fraction at 70°, and the C₈-C₁₀-fractions at 100-105°C.

Bruun and Hicks-Bruun¹⁴ produced pure normal hexane by treating narrow hexane fractions with chlorosulfonic acid (1:1 by volume) at 40-60°C for 12 hours. The sludge was then replaced with fresh acid and treated at 60°C. Almost pure normal hexane was obtained by this method.

Thus complete removal of isoparaffins and other tertiary hydrocarbons

by reaction with chlorosulfonic acid is quite feasible, but the selectivity of this method is questionable. Even under the mildest conditions of this treatment (which *per se* is not mild at all), some straight chain-paraffins are involved in the reaction. Thus it is rather doubtful that it can be used for quantitative determination of normal paraffins. The percentage of normal paraffins determined by this method would be too small, compared with the actual percentage, at the expense of the normal paraffins attacked by the reagent. On the other hand, this reaction can be successfully used for purification and identification of normal paraffins in suitably narrow fractions.

It is of interest that even 95 per cent sulfuric acid slowly reacts with highly branched paraffins, as has been shown by Whitmore and Johnson.¹⁰⁰ They treated 2,2,4-trimethylpentane with 95 per cent sulfuric acid at 20°C for ten days. Less than 25 per cent of the original compound was recovered.

The reaction between high molecular weight paraffins, particularly solid paraffin waxes, and fuming sulfuric or chlorosulfonic acid has frequently been used to evaluate the branching of hydrocarbons. It should be noted, however, that any systematic investigations of the reaction between individual high molecular weight paraffins and the above acids are entirely lacking. Thus conclusions based on the reactions in question and relating to high molecular weight paraffins should be considered open to some criticism.

It is well known that paraffin wax is much more stable toward fuming sulfuric or chlorosulfonic acid than is ceresin. The former (30 per cent SO_3) is more reactive than chlorosulfonic acid, and is preferably used for the treatment of solid paraffin hydrocarbons. Holde and Schünemann⁵² developed a method of computing the content of paraffin wax in commercial ceresins: 5 gr of ceresin are mixed with 20 cc of fuming sulfuric acid and heated for 5 minutes in a shale 10 cc in diameter on a steam bath. Paraffin wax is almost inert under these conditions, whereas ceresin reacts violently, with foam formation, evolution of sulfur dioxide and partial asphaltization and coke formation. When the reaction ceases, the reaction mixture is cooled to room temperature, and the cake of paraffin wax is separated, washed with water, dried and dissolved in gasoline in the presence of 3 gr of Fuller's earth. The authors showed that a Rumanian ceresin loses 70 per cent in the treatment, whereas paraffin waxes lose only from 3 to 7 per cent. Sachanen and Sherdeva¹²² found that a Surachany ceresin, after treatment on a steam bath with an 8-fold amount of fuming sulfuric acid, lost 25 per cent; a paraffin wax lost only 0.9 per cent under the same conditions. By using a large excess of fuming sulfuric acid (36-fold) it was possible to destroy up to 77 per cent of the ceresin.

The difference in the behavior of paraffin waxes and ceresins toward fuming sulfuric acid is usually explained by the difference in their structure. Paraffin waxes are considered to consist of normal paraffin hydrocarbons which are not attacked by fuming sulfuric acid. On the contrary,

ceresins are thought to be composed of isoparaffins. As will be seen in Chapter 6, this conception is in accord with numerous data on the chemical structure of petroleum waxes. It should be repeatedly pointed out, however, that the reaction with fuming sulfuric acid is rather qualitative, and cannot be used for the quantitative separation of high molecular weight isoparaffins from normal hydrocarbons.

Antimony Pentachloride

Antimony pentachloride is another reagent for removing isoparaffins and other tertiary hydrocarbons. Aromatics and unsaturates are attacked by it; thus they must be removed before the treatment with antimony pentachloride.

Schaarschmidt¹²⁶ found that antimony pentachloride reacts rapidly with all hydrocarbons containing tertiary hydrocarbon atoms. On the contrary, normal paraffins, quaternary paraffins, cyclohexane, cyclopentane and their 1,1-dialkyl derivatives are rather inert toward antimony pentachloride. If the temperature is raised, for instance, 80°C or higher, many hydrocarbons of the second group may react with antimony pentachloride. Thus low temperatures, (below 0°C) are used for separating isoparaffins or naphthenes of the tertiary structure.

Schaarschmidt and Marder¹²⁷ showed further that hydrocarbons which are inert toward antimony pentachloride at low temperatures become partially involved in the reaction with antimony pentachloride when mixed with tertiary hydrocarbons (chemical induction). This fact lessens the value of the method considerably. However, the portion of the non-tertiary hydrocarbons involved in the reaction at adequately low temperatures seems to be of minor importance, and the method may give an approximate evaluation of the content of tertiary hydrocarbons.

It should be kept in mind that the Schaarschmidt method cannot be used for determining isoparaffins in gasolines in view of the reaction between alkyl naphthenes and antimony pentachloride, as has been stated above. In purely paraffinic mixtures, such as alkylates, the quaternary isoparaffins, if present, are not determined by the method.

The reaction between tertiary hydrocarbons and antimony pentachloride is accompanied by formation of hydrogen chloride and crystalline double compounds of chlorinated tertiary hydrocarbons and antimony trichloride. Two moles of antimony pentachloride are consumed per mole of a tertiary hydrocarbon. Antimony pentachloride is added drop by drop while the sample is cooled to the required temperature, usually 0°C. The mixture is stirred, the hydrogen chloride formed being removed through a special tube. In some cases the reaction between tertiary hydrocarbons and antimony pentachloride starts only after a rather prolonged time, after which the reaction may be very violent and even explosive. This can be avoided by adding a small amount of the reaction products formed by a separate reaction of the product with antimony pentachloride at a higher temperature.

Moldavsky and Livshitz⁹³ modified somewhat the Schaarschmidt procedure, but Bauer⁷ could not reproduce the results obtained by Moldavsky and Livshitz.

Oxidation

Oxidation of petroleum fractions and hydrocarbons separated from them for identification purposes has been used in comparatively few cases. Oxidation of paraffins and naphthenes at moderate temperatures is accompanied by partial cracking and produces a number of oxidation products, such as alcohols, ketones, aldehydes, and acids, which may have only a remote resemblance to the initial hydrocarbons. Thus, Wiezevich and Frolich¹⁶¹ oxidized pentanes at 465°C under pressure and obtained acetic acid, acetone and a series of alcohols from methyl to amyl, as well as other oxidation products. They also oxidized heptanes under somewhat milder conditions and produced mainly hexyl and heptyl alcohols, indicating less degradation than in the case of pentanes.

In some cases, however, oxidation of paraffins at moderate temperatures yields only few acids. Francis, Piper and Malkin³⁵ oxidized a paraffin wax with air at 100°C and obtained between 58 and 70 per cent of acids and oxyacids. Of this mixture of acids, from 17 to 20 per cent were monobasic. Purification of these acids was carried out by extracting the strong alkaline aqueous-alcohol solution with light petroleum spirit and by subsequent conversion of the acids into methyl esters or lead salts, which were recrystallized. The acids regenerated from the methyl esters or lead salts were normal fatty acids, proving that the structure of the parent hydrocarbons of the paraffin wax was normal. It should be pointed out, however, that this conclusion seems not quite consistent with the comparatively small yield of normal fatty acids. Thus the possible existence of other structures in petroleum waxes cannot be excluded by the isolation of normal fatty acids in small yields.

Oxidation of benzene and naphthalene hydrocarbons, producing well defined crystalline acids, has been successfully used for identification of appropriate hydrocarbons in petroleum fractions. The cyclohexane hydrocarbons may be dehydrogenated into corresponding benzene hydrocarbons, which may be further oxidized to acids.

Oxidation of paraffinic side chains of aromatic hydrocarbons to carboxyl groups can be effected by various oxidizers, including nitric acid (1 vol. of concentrated nitric acid and 2-3 volumes of water), chromic acid (potassium bichromate and sulfuric acid), and potassium permanganate. The latter must be preferred to other agents. Nitric acid usually oxidizes only one paraffinic side chain, forming alkylated benzoic acids, which cannot be easily identified. Chromic acid in some cases may oxidize completely to carbon dioxide and water, as in the case of ortho-xylene. Potassium permanganate in alkaline solution under proper conditions oxidizes all side chains to carboxylic groups, *i.e.*, produces benzoic acid from all monoalkylated derivatives, phthalic acid from all dialkyl

benzenes, etc. The yield of the acids, however, is not quantitative; it does not exceed 30 per cent for toluene and ethylbenzene. Identification of the acids formed is comparatively simple on the basis of their melting points, particularly for benzoic acid (121.5°C), orthophthalic acid (in a sealed tube 191°C), metaphthalic acid ($345\text{--}347^{\circ}\text{C}$ in a sealed tube), and paraphthalic acid (sublimed at approximately 300°C without melting).

The procedure of oxidation by potassium permanganate is as follows. One gram of the hydrocarbon to be tested is mixed with 4 grams of potassium permanganate in 80 cc of water in the presence of one pellet of sodium hydroxide. Two or 3 grams of the hydrocarbon and correspondingly greater amounts of potassium permanganate and water are recommended. The oxidation takes place under reflux for 4 to 5 hours. Then the reaction mixture is cooled, acidified with dilute sulfuric acid and refluxed for another half hour. After this the mixture is cooled again, and the manganese dioxide formed is dissolved by the addition of sodium bisulfite. The acids formed are extracted with ether and liberated after evaporation of the ether. They are then treated with chloroform, which dissolves benzoic acid, whereas phthalic and other polyacids are insoluble in this solvent. Benzoic acid and acids insoluble in chloroform are recrystallized from ethyl alcohol.

The oxidation of alkyl benzenes for identification purposes is successfully used for the homologs of benzene. Oxidation of these hydrocarbons under appropriate conditions does not affect the ring structure. Oxidation of naphthalene derivatives, as well as of tricyclic aromatics, is frequently accompanied by partial rupture and oxidation of the rings. As a result, for instance, orthophthalic acid or phthalic anhydride is produced by oxidation of naphthalene or methylnaphthalenes. Under certain conditions, however, alkyl naphthalenes may form corresponding acids without ring rupture. Monoalkyl naphthalenes would form α -naphthoic acid (mp 161°C) or β -naphthoic acid (mp 184°C) depending upon the position of the alkyl group in the naphthalene molecule.

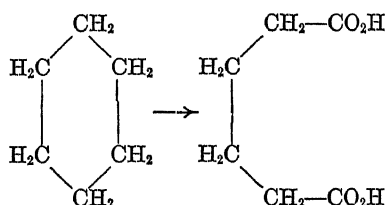
Tausz¹⁴⁰ oxidized the xylene fractions of various crudes and isolated all three phthalic acids, proving the presence of three xylenes. Carpenter¹⁵ oxidized the aromatic fractions separated from a Burma oil with aqueous alkaline solution of potassium permanganate. Oxidation of the fractions boiling between 125 and 150°C gave a good yield of crystalline material melting at about 280°C , i.e., phthalic acids. The acids were converted into dimethyl esters which were recrystallized from methyl alcohol, and gave two main fractions having melting points at 62 and 139°C respectively, corresponding to the methyl esters of meta- and paraphthalic acids (melting points 64 and 140°C , respectively). Thus the presence of meta- and paraxylenes has been proved.

The aromatic fractions from the same crude boiling above 210°C were oxidized by the same method and gave crystalline substances corresponding to α -naphthoic (mp 161°C) and β -naphthoic acids (mp 184°C), as well as to ortho and paraphthalic acids. Thus the fractions in question

contain the monoalkylated derivatives of naphthalene and ortho- and paradialkyl derivatives of benzene.

Kasansky and Markosova⁶¹ identified an octonaphthene separated from a Surachany gasoline by dehydrogenation into aromatics and by oxidation of the latter, which produced orthophthalic, metaphthalic and paraphthalic acids. Thus the octonaphthene was a mixture of ortho-, para- and predominantly metadimethylcyclohexane.

The oxidation of naphthenes, substituted or unsubstituted, by nitric acid is accompanied by the rupture of the ring and the formation of dibasic aliphatic acids, as, for instance,



Thus cyclohexane produces adipic acid and a small amount of glutaric acid; cyclopentane yields succinic and glutaric acids, etc. The reactions are far from quantitative. The oxidation of cyclohexane, however, gives a high yield of adipic acid, up to 50 per cent of theoretical. Concentrated nitric acid, at least 1.4 specific gravity, is used for the oxidation carried out at the boiling temperature of cyclohexane with reflux (Markownikoff,⁶⁰ Aschan⁴). From 4 to 6 parts of nitric acid are used for one part of cyclohexane. The reaction is slow, requiring about 10 hours. After it has been completed, the excess of nitric acid and the unreacted hydrocarbon are distilled off. The residuum is evaporated on a steam bath until the nitric acid is completely removed. The product obtained contains adipic acid and a small proportion of glutaric acid.

When concentrated nitric acid is employed, the nitration is negligible. The small amount of nitrocyclohexane formed is evaporated with the excess of nitric acid and unreacted cyclohexane. A weak acid has a nitrating effect (page 154).

The conditions for oxidation of other naphthenes with concentrated nitric acid are similar to those given above, but the reaction time may be longer. The nitration reactions may interfere with the oxidation to dibasic acids to a greater extent than in the case of cyclohexane.

Oxidation of alkylated naphthenes may produce monobasic acids in addition to dibasic acids, as the result of attacking the paraffinic side chains. For instance, Kishner⁶⁷ showed that the oxidation of methylcyclopentane by nitric acid yields glutaric, succinic, acetic and formic acids.

Zalkind and Huskivadze¹⁶⁵ investigated the oxidation of decalin and butyldecalin with strong nitric acid. Glutaric and oxalic acids, in yields of 10 and 7.4 per cent, respectively, were obtained on oxidation of decalin,

and adipic and glutaric acids on oxidation of butyldecalin. It is of interest that the oxidation of decalin with weak nitric acid of specific gravity 1.2 produces 6 per cent phthalic acid. Thus oxidation of bicyclic naphthenes by strong nitric acid forms mostly dibasic acids, as in the case of monocyclic naphthenes.

The fact that the oxidation of naphthenes by concentrated nitric acid produces various dibasic acids in comparatively moderate yields is a drawback to the application of this method to the identification of naphthenes. Zalkind and Huskivadze oxidized some naphthenic kerosene fractions (apparently from Baku crude oils) with concentrated nitric acid and produced adipic, glutaric and succinic acids. The total yield of the acids, chiefly of adipic and glutaric, amounted to 15 per cent under the most favorable conditions, in the presence of vanadium pentoxide. No conclusions as to the structure or content of the naphthenes can be drawn on the basis of these experiments.

Oxidation with ozone may be used for separation and to some extent for identification of unsaturates which react readily with this reagent. The first stage is formation of ozonides which in the second stage may be hydrolyzed into acids, aldehydes and other compounds.^{112a} The addition of ozone takes place at the double bond, and the formation of acids and aldehydes is the result of cracking of the ozonide at the same point. Identification of the acids and aldehydes formed would indicate the position of the double bond and structure of the original olefin. Unsaturated hydrocarbons with active double bonds react with ozone rapidly and quantitatively; the rate of ozonization of aromatic hydrocarbons is much slower. The successful application of the ozonization method to natural rubber by Harries indicates its potentialities; to the best knowledge of the author, it has not been used for separation and study of unsaturates in petroleum.

Oxidation of methyl groups carbon-linked to acetic acid may be promising as a method of determining the methyl groups in unknown hydrocarbons. Kuhn and L'Orsa,^{72a} found that under specific conditions chromic acid oxidizes methyl groups linked with carbon atoms almost quantitatively into acetic acid, which is stable toward this reagent. Consequently, the oxidation products of such hydrocarbons consist of carbon dioxide, water and acetic acid, which is distilled and titrated. Thus the number of methyl groups or paraffinic side branches in a hydrocarbon or fraction may be determined by this method. There are several exceptions to the general rule, including aromatic hydrocarbons forming benzoic acid. The method was discussed recently by Barthel and LaForge.^{6a}

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Chapter 4

Hydrocarbons of Straight-Run Distillates

The hydrocarbons of straight-run petroleum products have been studied for more than 80 years. A number of individual hydrocarbons have been separated and identified. Beilstein, Aschan, Markovnikoff, Zelinsky, Young and Mabery contributed much to the knowledge of these hydrocarbons in the early stages of these extensive investigations. Mabery also studied hydrocarbons of the high-boiling fractions and established the ring structure of the high molecular weight hydrocarbons composing lubricating oils and similar fractions.

The separation of individual hydrocarbons from petroleum fractions, particularly quantitative, is a difficult problem which so far has been solved only for comparatively low-boiling fractions, including the kerosenes of a few crude oils. High-boiling fractions could not be resolved into individual hydrocarbons, as will be seen later. For this reason, determination of various classes of hydrocarbons (paraffins, naphthenes and aromatics) or of sub-classes (cyclopentanes, cyclohexanes, isoparaffins) is of primary importance. It should also be pointed out that the commercial value of petroleum products is determined rather by their bulk chemical composition than by specific individual hydrocarbons. Thus gasolines having a high content of highly branched paraffins and aromatics are likely to have a high octane number. A motor oil of high viscosity index is rich in naphthenes with long paraffinic side chains, etc.

It seems certain, however, that the wide commercial segregation of individual hydrocarbons from liquid petroleum products is a problem of the near future. Such hydrocarbons as toluene, cyclohexane, methyleyclopentane, methylcyclohexane, and a series of normal paraffins may be produced commercially from straight-run gasolines.

Various Hydrocarbon Classes in Straight-run Gasolines

The chemical composition of straight-run gasolines has been studied more thoroughly and completely than that of other petroleum products and fractions. The problem is simplified by the absence of olefins and other unsaturates; only paraffins, naphthenes and aromatics are present in straight-run gasolines. Derivatives of cyclopropane, cyclobutane, cycloheptane, etc. have not been found in gasolines. The derivatives of bicyclic naphthenic and aromatic hydrocarbons (decahydronaphthalene, tetrahydronaphthalene, naphthalene) boil above the range of light gasolines and can be present only in heavy ends and heavy naphthas. Thus,

is it mainly the derivatives of cyclohexane, cyclopentane and benzene that represent the cyclic hydrocarbons of straight-run gasolines. The non-hydrocarbon constituents of gasolines will be discussed in Chapters 7 and 8. As has been pointed out, hydrocarbons constitute by far the most important part of straight-run and cracked gasolines—about 99 per cent of the total on the average.

The separation of individual hydrocarbons from straight-run gasolines by fractional distillation, crystallization and other physical and chemical methods has been carried out for a very limited number of gasolines or gasoline fractions because of the experimental difficulties of these operations. The determination of various classes of hydrocarbons (paraffins, naphthenes and aromatics) is much simpler, and has been performed for all important gasolines. The results of such determinations are summarized in this section.

As discussed in Chapter 2, the determination of aromatics in straight-run gasolines by sulfuric acid treatment and aniline points (or appropriate other physical properties, such as specific gravity, refractive index or intercept, etc.) gives fairly reliable results. The possible error in these determinations does not exceed 2 per cent of the total gasoline. The determination of naphthenes and paraffins on the basis of the same physical properties is less reliable, with a possible error up to 5 per cent. The data on the relative content of cyclopentane and cyclohexane derivatives are less accurate, because of the difficulties encountered in the behavior of dehydrogenation catalysts. There are no reliable methods of determining the total content of isoparaffins. Thus the following data contain the percentage of aromatics, naphthenes and paraffins, as well as of cyclopentanes and cyclohexanes in available cases.

There are some discrepancies between the data of different authors. For instance, the percentage of aromatics in a Smackover gasoline determined by Tydeman and Kellogg was 18.0 per cent and by Garner and Evans only 2 per cent. Such a difference may be due to the higher end point of the gasoline used by Tydeman and Kellogg (207°C as compared to 150°C). It should be kept in mind that the 207°C end point gasoline from a heavy Smackover crude is particularly rich in naphtha fractions boiling from 150 to 207°C, which are very rich in aromatics. Another discrepancy in the chemical composition of a Turner Valley gasoline determined by Donald and Watson and Spinks has been discussed on page 108.

Gruse and Stevens³⁵ give the chemical composition of various gasolines determined by the Garner's method, *i.e.*, the use of nitric acid for separation of aromatics. Sulfuric acid for this purpose should be preferred to nitric acid, as discussed in Chapter 3. The figures for paraffin content given by Gruse and Stevens should be considered too high and those for naphthenes too low. For instance, the paraffin content of Mid-Continent gasoline is given as 72.9 per cent and of naphthenes as 22.0 per cent, as compared to 61 per cent and 29 per cent respectively (Table 48) and to 60 per cent and 30 per cent found by The Bureau of Standards. In

general, however, the agreement between the data of different authors referring to the same gasoline is satisfactory.

The distinction between the above classes of hydrocarbons present in gasolines is quite sharp. Naphthene-aromatic structures are absent in the hydrocarbons composing gasolines. In addition to this, the paraffinic side chains are short, not exceeding C_8 , and do not affect appreciably the aromatic or naphthenic character of hydrocarbons. Thus the application of ring analysis to straight-run gasolines does not present any advantage as compared with the total determination of aromatics, naphthenes and paraffins. From the commercial standpoint, the determination, for instance, of the aromatic hydrocarbons in a gasoline is more important than that of aromatic rings. Accordingly, the chemical composition of gasolines and gasoline fractions is usually determined by quantitative separation of aromatics and by evaluation of paraffins and naphthenes by the methods described in Chapter 2.

The percentage of aromatics in straight-run gasolines usually does not exceed 10 per cent in 400°E.P. gasolines, the remainder being paraffins and naphthenes (Tables 48-69). Straight-run gasolines containing 20 per cent or more of aromatic hydrocarbons are comparatively rare. Such are, for instance, Conroe, Mexia (Oklahoma), Burma and particularly Borneo gasolines. It is of interest that naphthenic gasolines are frequently poor in aromatics. Some paraffinic gasolines contain a larger proportion of aromatics than do naphthenic gasolines.

Aromatic hydrocarbons of gasolines, rich in these constituents, may be extracted by solvent, for instance, liquid sulfur dioxide, to produce highly aromatic concentrates or solvents. For instance, Borneo naphthas boiling in the range 143-186°C and containing 46-49 per cent aromatics, yield naphthas with an aromatic content up to 67 per cent.²⁰ According to Lazar,⁵⁴ commercial extraction of some California naphthas yields highly aromatic solvents (aniline point up to -12°C). Individual hydrocarbons such as toluene, cannot be manufactured commercially from straight-run gasolines, with the exception of highly aromatic crude oils.

Paraffins and naphthenes are the main components of straight-run gasolines. The percentage of paraffins and naphthenes depends upon the crude oil: paraffin-base and a few mixed-base crudes produce gasolines rich in paraffins. The proportion of paraffins in such gasolines is above 50 per cent and may be as high as 70 per cent. Pennsylvania, Rodessa, many Mid-Continent, some Mexican, Russian and other gasolines belong to this type and contain between 60 and 70 per cent paraffins. The intermediate type with a paraffin content of about 50 per cent is also quite common; it occurs in many gasolines of Texas, California, Mid-Continent, Mexico, and Russia. Such gasolines contain about 40 per cent naphthenes. Highly naphthenic gasolines, containing 60 per cent or more naphthenes, are comparatively rare. Certain Californian and Russian gasolines (Surachany or Balachany, Tables 55 and 59) have this high percentage of naphthenes.

There is a close relationship between the chemical composition of gas-

olines and that of other fractions. As a result, paraffin-base crudes yield paraffinic gasolines and naphthenic-base crudes naphthenic gasolines. There are, however, some exceptions to this general rule. For instance, naphthenic Santa Maria Valley (California) crude gives a paraffinic straight-run gasoline, whereas paraffinic Surachany crudes give highly naphthenic straight-run gasolines.

The distribution of paraffins, naphthenes and aromatics in various fractions of straight-run gasolines is identical for almost all gasolines (Tables 49, 50, 53, 54, 60). The percentage of aromatics increases with increasing boiling range of the fraction. The percentage of paraffins is very high in low-boiling fractions, and decreases steadily with increasing boiling range. This is partially due to the comparatively high boiling points of the lowest naphthenes and aromatics (49°C for cyclopentane and 80°C for benzene); hence oil field gases and low-boiling gasoline fractions cannot contain an appreciable amount of hydrocarbons other than paraffins. In addition to this, decrease in the content of paraffins with increasing boiling range is usually characteristic of all fractions, including high-boiling oils. In some cases the paraffin content is almost constant in different gasoline fractions or varies irregularly.

The percentage of naphthenes usually increases slightly with increasing boiling range, or remains almost constant.

It is understood that all the above conclusions concern fractions of comparatively large boiling ranges, as, for instance, from 30 to 50°C. The content of paraffins and other hydrocarbons in narrow fractions depends upon the content of individual hydrocarbons and does not conform to the regularities of the large fractions.

The distribution of cyclohexane and cyclopentane derivatives in straight-run gasolines varies from one crude to another. The data of Tables 55, 61, and 62 show that in general neither cyclopentanes nor cyclohexanes predominate in straight-run gasolines or in their fractions. Some narrow fractions of Surachany gasolines are particularly rich in the derivatives of cyclohexane, as the data of Zelinsky and Shuikin²⁵ show (Table 63). These authors obtained fractions containing more than 50 per cent aromatics by catalytic dehydrogenation of the above original fractions in the presence of nickel on alumina or platinum on charcoal.

According to the data of Danaila and Stoenescu²⁸ (Table 66), however, the percentage of cyclohexanes in Rumanian straight-run gasolines is small, so that cyclopentane derivatives should be predominant in these gasolines.

The separation of individual hydrocarbons in a Ponca City and other gasolines (Tables 70, 72) confirms the fact that the derivatives of cyclopentane and cyclohexane are distributed approximately in equal amounts, at least in most gasolines.

It is well known that the octane number of a gasoline depends upon its chemical composition. Any computation of the octane number on this basis, however, is impossible because the octane number of paraffins and naphthenes greatly depends upon the molecular weight and the branch-

ing of hydrocarbons. As a result, for instance, the octane number of normal pentane is very high (63 by the Motor method) as compared with that of other normal paraffins (−53 for normal decane). The octane number of isomeric octanes varies from −19 (normal octane) to 105 (2,2,3-trimethylpentane), depending on the degree of branching. The high octane number of cyclohexane (80) drops to −7 for normal amylhexane. Only for aromatic hydrocarbons boiling in the range of gasolines, is the octane number comparatively constant, exceeding 100.

Text cont'd on p. 208

Table 48. Chemical Composition of Straight-run Gasolines.*

Crude Oil	Specific Gravity (D ₁₅ ²⁰)	End Point (°C)	Per Cent by Wt of		
			Aromatics	Naphthenes	Paraffins
Oklahoma City, Okla.	0.739	177	10	29	61
Tonkawa, Okla.	0.736	150	9	35	56
" "	0.750	210	12	37	49
Davenport, Okla.	0.725	150	8	28	64
" "	0.740	210	11	28	61
East Texas	0.714	159	6	42	52
Mexia, Texas	0.750	150	22	21	57
" "	0.764	210	18	21	61
Rodessa, La.	0.719	160	10	20	70
Santa Fé Springs, California	0.735	151	10	50	40
Kettleman Hills, California	0.720	151	8	45	47
Signal Hill, Calif.	0.735	153	6	52	42
Huntington Beach, California	0.727	155	7	49	44
" " "	0.755	210	11	54	35
Turner Valley, Canada	0.726	150	11	38	51
" " "	0.741	200	15	35	50

*Method of determination: treatment by sulfuric acid and determination of aniline points.^{31, 32}

Table 49. Chemical Composition of Pennsylvania Straight-run Gasoline.*
(61.7 API Gravity, Boiling Range 102° to 405°F, ASTM Octane Number 44)

Fraction (°C)	Percentage of		
	Aromatics	Naphthenes	Paraffins
Gasoline	7	18	75
38-70°	0	3	97
70-100°	4	18	76
100-150°	8	22	70
Bottoms	12	26	62

*Method of determination: aromatics by dispersion, paraffins and naphthenes by refractive index.^{33a}

Table 50. Content of Aromatics in American Straight-run Gasolines.³²

Crude Oil	Yield of Gasoline	Per Cent by Wt of			
		Benzene	Toluene	Xylenes	Total Aromatics up to 150°C
Texas, Powell	16	0.4	1.2	2.9	4.5
Oklahoma, Reagan	35	0.1	0.2	1.5	1.8
Oklahoma, Seminole	36	0.1	0.6	1.5	2.2
California	20	0.6	2.4	3.7	6.7
Texas, Mexia		5.0	8.0	4.5	17.5
Ark., Smackover, heavy		0.15	0.4	1.5	2.05
Mexico, Panuco	3	0.7	1.9	4.0	6.6
Mexico	10	0.5	1.5	3.7	6.1
Venezuela	7	0.9	1.5	3.7	6.1
Colombia	20	0.2	0.8	1.3	2.3
Peru	20	0.3	1.6	2.5	4.4

Table 51. Content of Aromatics in Mid Continent Straight-run Gasolines.*

Crude Oil	the Gravity Gasoline at 15°C	Boiling Range (°C)	Percentage of Aromatics by Weight
Seminole, Okla.	0.737	38-203	0.7
Yale, Okla.	0.755	49-206	7.3
Lucien, Okla.	0.738	39-204	11.0
Upton, W. Texas	0.759	49-206	17.3
Pecos, W. Texas	0.766	46-208	13.9
Hobbs, N. Mexico	0.746	47-207	10.7
Caddo, La., light	0.749	94-207	4.0
Caddo, La., heavy	0.840	149-212	4.5
Smackover, Ark., light	0.762	64-204	16.4
Smackover, Ark., heavy	0.778	72-207	18.0
Longview, E. Texas	0.741	41-205	9.6
Luling, S. W. Texas	0.775	122-206	2.1

*Method of determination: aniline points before and after the treatment by sulfuric acid.¹⁰³

Table 52. Content of Aromatics in U. S. Straight-run Gasolines (E.P. 180°C).*

Gasoline	Aromatic Content (% by weight)
Ponca, Oklahoma	9.8
East Texas	10.4
Bradford, Pennsylvania	8.3
Greendale-Kawkawlin, Mich.	7.2
Winkler, Texas	4.9
Midway, Calif.	8.0
Conroe, Texas	27.6

cent.²⁹on: adsorption. Possible deviations from the above figures ± 0.2 to 0.5 perTable 53. Chemical Composition of Gasoline Fractions.
U. S. Straight-run Gasolines.*

Boiling Range of Fraction (°C)	Specific Gravity at 15°C	Per Cent by Wt of		
		Aromatics	Naphthenes	Paraffins
<i>Mexia, Oklahoma</i>				
60-95	0.734	29	17	54
95-122	0.749	21	22	57
122-150	0.758	19	23	58
150-200	0.772	16	21	63
<i>Tonkawa, Oklahoma</i>				
60-95	0.708	6	26	68
95-122	0.737	8	34	58
122-150	0.756	12	43	45
150-200	0.782	20	41	39
<i>Davenport, Oklahoma</i>				
60-95	0.699	5	21	74
95-122	0.733	7	28	65
122-150	0.751	12	33	55
150-200	0.773	16	29	55
<i>Huntington Beach, California</i>				
60-95	0.701	4	31	65
95-122	0.747	6	48	46
122-150	0.766	11	64	25
150-200	0.794	17	61	22

*Method of determination: treatment by sulfuric acid and measuring of aniline points.¹⁰³

Table 54. Chemical Composition of Gasoline Fractions.
Canadian Straight-run Gasoline (Turner Valley).*

Boiling Range of Fraction (°C)	Specific Gravity at 20°C	Per Cent by Vol of—		
		Aromatics	Naphthenes	Paraffins
21-50	0.635	0	0	100
50-75	0.6745		17.0	83.0
75-100	0.7197	1.9	53.9	44.2
100-125	0.746	11.0	58.3	30.7
125-150	0.766	29.1	23.4	47.5
150-175	0.779	28.5	19.3	52.2
175-200	0.790	19.4	39.2	41.4
200-225	0.8023	13.3	47.3	39.4

*Method of determination: treatment by sulfuric acid and measuring of aniline points. A parallel determination by the Kurtz method gives reasonably close results.²²

Table 55. Chemical Composition of Light Paraffin-Naphthene Fraction, 40° to 102°C, of U. S. Straight-run Gasolines.*

Gasoline	Normal Paraffins	—Percentage by Vol—		
		Isoparaffins	Cyclopentanes	Cyclohexanes
Ponca, Okla.	35.7	20.5	23.4	20.4
East Texas	24.7	27.3	26.0	22.0
Bradford, Pa.	34.4	32.2	13.4	20.0
Greendale-Kawkawlin, Mich.	63.1	13.2	8.0	15.7
Winkler, Texas	9.5	61.6	8.4	20.5
Midway, Calif.	10.0	21.5	41.0	27.5
Conroe, Texas	18.2	20.3	17.3	44.2

*Method of determination: fractionation and separation of individual hydrocarbons.²³

Table 56. Chemical Composition of Mexican Straight-run Gasolines.*

Crude Oil	Specific Gravity at 60°/60°F	Boiling Range (°C)	Per Cent by Wt of—		
			Aromatics	Naphthenes	Paraffins
Altamira	0.762	40-200	14.4	37.2	48.4
San Marcos	0.746	58-185	14.7	41.0	44.3
Juan Casiano	0.723	53-182	8.7	33.8	57.5
Potrero	0.727	50-200	9.2	35.4	55.4
Zakamixtle	0.723	49-187	8.9	33.7	57.4
Mecatepec	0.727	51-200	8.1	36.8	55.1
Furbero	0.730	51-189	10.7	38.3	51.0
Teapa	0.720	50-201	6.0	32.0	62.0
Tecunapa	0.736	50-158	5.4	50.0	44.6

*Method of determination "conventional" (apparently treatment with sulfuric acid and aniline points).²⁴

Table 57. Content of Aromatics in Argentine Straight-run Gasolines.²⁵

Crude Oil	Specific Gravity at 15°C	Boiling Range (°C)	Aromatics (% by weight)
Commodore Rivadavia, Type I	0.755	67-200	13.5
Commodore Rivadavia, Type II	0.742	66-198	9.0
Commodore Rivadavia, Type III	0.764	70-200	13.5

Table 58. Content of Aromatics in Trinidad Straight-run Gasolines, E.P. 145°C.²²

	Specific Gravity of Crude Oil—		
	0.9593	0.9169	0.8627
Benzene	0.1	0.5	1.7
Toluene	0.4	0.6	6.8
Xylenes and ethylbenzene	0.2	1.9	9.5
Total	0.7	3.0	18.0

Table 59. Chemical Composition of Russian Straight-run Gasolines.*

Crude Oil	Specific Gravity at 15°	End Point (°C)	Per Cent by Wt of		
			Aromatics	Naphthenes	
Baku, Surachany†	0.790	200	8.6	64.4	27.0
" "	0.760	175	3	71	26
" "	0.760	150	1.4	70	28
Baku, Balachany†	0.785	200	6.4	68.6	25.0
" "	0.756	175	2	65	33
Baku, Bibi-Eibat†	0.775	200	8	63	29
" "	0.742	175	4	53	43
" "	0.740	150	0.8	55	44
Baku, Binagady†	0.790	200	12.5	64.4	23.1
" "	0.747	175	5	50	45
" "	0.745	150	3.2	53	43
Baku, Blended†		150	3.3	57.9	38.8
Grozny, New Oil Field†	0.741	200	8	29	63
" "	0.722	175	6	29	65
" "		130	4	27	69
" "		150	5.0	28.5	66.5
Grozny, Old Oil Field†	0.761	200	13	47	40
" "	0.742	175	10	43	47
Maikop†	0.751	200	16	38	46
" †	0.725	130	8	33	59
" †		150	13.3	33.8	50.7
Sterlitamak†			16	24	60
Chusov†			46	24	30

fractions and rich in heavy fractions.

†Method of determination: treatment with sulfuric acid and measuring of aniline points.^{93, 94, 105}‡Method of determination: fractionation followed by chemical methods.¹⁰⁶

Table 60. Chemical Composition of Fractions of Russian Straight-run Gasolines.*

Boiling Range of Fraction (°C)	Specific Gravity at 15°C	Per Cent by Wt of		
		Aromatics	Naphthenes	Paraffins
<i>Grozny, New Field</i>				
60-95	0.706	4	34	62
95-122	0.737	6	37	57
122-150	0.757	9	30	61
150-200	0.782	14	29	57
<i>Grozny, Old Field</i>				
60-95	0.708	5	39	56
95-122	0.746	9	48	43
122-150	0.767	13	45	42
150-200	0.798	21	55	24
<i>Baku, Surachany</i>				
60-95	0.743	0	76	24
95-122	0.760	1	81	18
122-150	0.779	6	51	43
150-200	0.810	17	66	17
<i>Baku, Balachany</i>				
60-95	0.726	0	56	44
95-122	0.762	1	68	31
122-150	0.781	6	66	28
150-200	0.805	12	75	13
<i>Baku, Bibi-Eibat</i>				
60-95	0.724	3	50	47
95-122	0.750	3	50	37
122-150	0.773	7	57	31
150-200	0.808	12	69	19

Table 60. Chemical Composition of Fractions of Russian Straight-run Gasolines.*
(Continued)

Boiling Range of Fraction (°C)	Specific Gravity at 15°C	-Per Cent by Wt of-		
		Aromatics	Naphthenes	Paraffins
<i>Emba, Dossor</i>				
60-95	0.705	4(?)	40	56
95-122	0.747		63	36
122-150	0.771		57	39
150-200	0.799		69	24
<i>Perm, Ural</i>				
60-95	0.734	20	41	39
95-122	0.796	51	27	22
122-150	0.823	62	18	20
150-200	0.826	60	15	25

Method of determination: treatment with sulfuric acid and measuring of aniline points.

Table 61. Chemical Composition of Fractions of Russian Straight-run Gasolines.*

Boiling Rang of Fraction (°C)	Specific Gravity at 15°C	-Per Cent by Wt of-			
		Aromatics	Cyclohexanes	Cyclopentanes	Paraffins
<i>Baku, Balachany</i>					
60-95	0.731	0	33	29	38
95-122	0.760	1.5	49	27	22.5
122-150	0.776	4	40	32	24
<i>Baku, Surachany</i>					
60-95	0.736	0	37	36	27
95-122	0.757	1	47	33	19
122-150	0.764	6	38	30	26
<i>Baku, Bibi-Eibat</i>					
95-122	0.750	3	33	27	37
122-150	0.773	7	20	41	32
<i>Emba, Dossor</i>					
95-122	0.749	2	23	37	38
122-150	0.766	4	33	26	37
<i>Grozny, New Field</i>					
60-95	0.713	3	11	26	60
95-122	0.741	7	14	22	57
122-150	0.760	9	8	22	61
<i>Grozny, Old Field</i>					
60-95	0.710	4	17	25	54
95-122	0.744	8	29	16	47
122-150	0.766	12	24	23	41

*Method of determination: treatment with sulfuric acid, measuring of aniline points and catalytic dehydrogenation of cyclohexanes.²¹

Table 62. Chemical Composition of Fractions of Russian Straight-run Gasolines.*

Boiling Range of Fraction (°C)	-Per Cent by Wt of-			
	Aromatics	Cyclohexanes	Cyclopentanes	Paraffins
<i>Sterlitamak, Ural</i>				
60-95	10	6	13	71
95-122	10	12	16	62
122-150	13	18	14	55
150-200	28	23	14	35
<i>Uchta, Ural</i>				
95-122	4	16	31	49
122-150	5	15	48	32
150-200	5	21	64	10

Table 62. Chemical Composition of Fractions of Russian Straight-run Gasolines.*
(Continued)

Boiling Range of Fraction (°C)	Per Cent by Wt of—			
	Aromatics	Cyclohexanes	Cyclopentanes	Paraffins
<i>Kala, Baku</i>				
60-95	0	26	37	37
95-122	1	42	29	28
122-150	3	43	37	17
150-200	10	36	43	11

*Method of determination: treatment with sulfuric acid, aniline points and catalytic dehydrogenation of cyclohexanes.¹²⁴

Table 63. Chemical Composition of Fractions of Surachany Straight-run Gasoline.*

Boiling Range of Fraction (°C)	Per Cent by Wt of—			
	Aromatics	Cyclohexanes	Cyclopentanes	Paraffins
118-120	1.0	56.2	15.5	27.3
120-124	1.7	56.9	15.7	25.7
124-130	4.0	54.3	20.0	21.7
130-140	5.0	44.6	23.2	27.2

*Method of determination: treatment with sulfuric acid and measuring of aniline points, catalytic dehydrogenation of cyclohexanes.¹²⁵

Table 64. Content of Aromatics in Rumanian Straight-run Gasolines.²⁸

Crude Oil	Per Cent by Wt of Aromatics
Ochiuri, asphaltic base, 0.877	4
Bustenari, asphaltic base, 0.855	6
Moreni, asphaltic base, 0.852	11
Zemes, mixed base, 0.868	8
Mionesti, mixed base, 0.889	9
Solont-Stanesti, mixed base, 0.855	10
Campina, mixed base, 0.852	4
Arbanesi, waxy, 0.826	21
Ceptura, waxy, 0.879	6
Filipesti, waxy, 0.887	8
Moreni, waxy, 0.801	12
Ochiuri, waxy, 0.852	3
Gura-Ocnisei	7.5

Table 65. Chemical Composition of Rumanian Straight-run Gasolines,
Boiling Range 50°-150°C.*

Crude Oil	Specific Gravity at 15°C	Per Cent by Wt of—		
		Aromatics	Naphthenes	Paraffins
Merisor	0.7362	7.9	53.6	38.5
Bucsan	0.7365	12.1	30.1	54.2

*Method of determination: fractionation followed by chemical treatment.⁸⁴

Table 66. Chemical Composition of Fractions of Rumanian Straight-run Gasolines.¹⁸

Boiling Range (°C)	Per Cent by Wt of—	
	Aromatics	Cyclohexanes
<i>Bustenari, Oligocen</i>		
65-95	3.28	12.77
95-115	4.98	3.82
115-145	10.06	3.76

Table 66. Chemical Composition of Fractions of Rumanian Straight-run Gasolines.¹⁸
(Continued)

Boiling Range (°C)	Aromatics	Cyclohexanes
<i>Moinești</i>		
65-95	7.08	4.23
95-115	7.94	2.66
115-145	11.36	4.23
<i>Bustenari, Miocen</i>		
65-95	4.34	17.46
95-115	3.55	8.47
115-145	9.69	3.37
<i>Moreni</i>		
65-95	8.36	12.12
95-115	11.12	8.48
115-145	15.30	3.08
<i>Bustenari, Miocen</i>		
65-95	4.34	17.46
95-115	3.55	8.47
115-145	9.69	3.37

Table 67. Chemical Composition of Polish Straight-run Gasolines (E.P. 180°)

Crude Oil	Specific Gravity at 15°C	Per Cent by Wt of		
		Aromatics	Naphthenes	Paraffins
Potok	0.744	10	27	63
Grabovnica	0.743	7.5	27	65.5
Harklova	0.749	6.5	36	57.5
Kroszienko	0.772	21	36.5	42
Veglovka	0.741	3	43	54
Rowne Rogi	0.749	12	29.5	58.5
Urysz	0.750	7	30	62
Dziunia Schodnica	0.754	10	28.5	61.5
Jaszczew	0.759	11.5	19	68.5
Ferdinand Schodnica	0.741	6.5	33.5	60
Wankowa	0.746	12	26	61.5
Rypne	0.756	6.5	22.5	70
Bitkow 45	0.743	7.5	16.5	76
Bitkow 113	0.759	8.5	19	72.5
Chrobry 3	0.767	14	13	73
Chrobry 4	0.745	8	21	70.5
Boxal	0.741	12.5	25.5	61
Konrad	0.745	12	26	61
Herzfeld	0.747	13	24	62
Joffre 5	0.757	14	24	61
Petain	0.759	14.5	21	63.5

*Method of determination: treatment with sulfuric acid and measuring of aniline points.²⁴Table 68. Aromatics in Fractions of Burma Straight-run Gasoline and Kerosene.¹⁴

Boiling Range (°C)	Per Cent by Volume of Aromatics	Aromatics
below 125	11.5	Benzene and toluene
125-150	18.3	Mostly xylenes, predominantly meta-xylene.
150-180	19.9	Paracymene, cumene, pseudocumene, mesitylene
180-210	18.5	
210-230	18.1	{ No naphthalene; derivatives of benzene and naphthalene
230-250	19.4	
250-275	24.2	

Table 69. Content of Aromatics in Asiatic Straight-run Gasolines.^{46, 123}

Crude Oil	Specific Gravity at 15°C	Boiling Range (°C)	Per Cent by Wt of			
			Benzene	Toluene	Xylenes	Total Aromatics up to 150°C
Borneo			7	14	15	36
Sarawak, Miri	0.765	60-180	0.4	1.9	1.5	3.8
Burma	0.757	58-161	2.9	6.0	6.8	15.7
Badarpur	0.758		1.0	1.6	2.9	5.5
Digboi (% by vol)			4.6	7.3	7.6	19.5

Individual Hydrocarbons in Straight-run Gasolines

As has been mentioned above, a series of individual hydrocarbons was isolated and identified by Beilstein, Aschan, Markovnikoff, Zelinsky, Young, Mabery and their co-workers, as well as by other early workers. The importance of these investigations cannot be underestimated. As a matter of fact, the present knowledge of the hydrocarbons of gasolines and crude oils does not differ fundamentally from the general conceptions developed by the authors cited. Further development of petroleum chemistry has been going on by evolution rather than by revolution, bringing about radical changes in the earlier conceptions.

The petroleum hydrocarbons identified in the earlier classical studies mentioned above are not listed in this chapter mainly because of the lack of any data on the quantities involved. Quantitative methods of separating hydrocarbons were developed much later, during the last 15 years. The list of hydrocarbons identified in petroleum without their relative quantities in corresponding gasolines or crude oils, hardly has any great interest at the present time. In addition to this, all hydrocarbons identified by the earlier workers have been reidentified in recent studies and determined quantitatively with more or less accuracy.

As discussed in Chapters 2 and 3, fractionation of petroleum, mostly by distillation and to a lesser extent by crystallization, is the basic method for quantitative separation of individual hydrocarbons. Other physical and chemical methods described in Chapters 2 and 3 should be considered as auxiliary methods for final separation and identification. Thus the problem in question involves the use of large amounts of crude oils or gasolines for a series of fractionations, as well as the use of very efficient fractionating columns.

It should be repeatedly pointed out that the application of the methods of infrared and Raman spectra and of mass spectroscopy to very narrow petroleum fractions, produced by efficient distillation and other fractionation methods, should give most promising results. These methods are still in their infancy, and are limited to special problems, such as the analysis of C_4 -fractions, alkylates, etc.

The most successful and complete separation of individual hydrocarbons has been carried out by the National Bureau of Standards for a gasoline from Ponca City (Oklahoma) crude. This may be considered as a typical Mid-Continent crude of the so-called mixed-base type. The

methods of separation have been described in detail in Chapters 2 and 3, and the results obtained are summarized in Tables 70 and 71. More than 40 individual hydrocarbons have been separated from the gasoline fraction boiling between 55° and 180°C. The separation was much closer than in all other similar studies. As a matter of fact, many hydrocarbons separated from the Ponca City gasoline were obtained in a purer state than they were known before this investigation. Over 75 per cent of the gasoline boiling between 55° and 145°C and over 33 per cent of the naphtha boiling between 145° and 180°C were assigned to the individual hydrocarbons separated. The respective amounts of paraffins, naphthenes, and aromatics separated (60:30:10) are very close to those for other Mid-Continent gasolines (Oklahoma City, Tonkawa, Davenport, see Table 48), which have been investigated by the methods of bulk hydrocarbon analysis without separation of individual hydrocarbons.

The composition of straight-run gasolines seems to be simpler than might be expected on the basis of the numerous isomers which might be present in the boiling range of the gasolines. As Rossini stated, "Three-fourths of the gasoline fraction 55°-145°C is constituted by approximately 31 hydrocarbons, one-half by about 8, one-third by 4, and one-fifth by 2. That is to say, while there may actually be thousands of hydrocarbons in this fraction, the major part of the material is made up of a rather small number of constituents."⁶⁹ Approximately 50 per cent of the 55°-180°C gasoline is composed of about 12 hydrocarbons.

Rossini *et al.*⁹² and Forziati *et al.*²⁹ have published the data on the composition of a series of most typical straight-run gasolines: Ponca (paraffinic), Conroe, Texas (high aromatic), Michigan (high paraffinic), Winkler, Texas (high isoparaffinic), Midway, California (high naphthenic), Pennsylvania (high paraffinic). These gasolines were investigated by simplified methods. They were separated by adsorption with silica gel into naphthenic-paraffinic and aromatic parts, which were fractionated in the columns described in Chapter 2. The aromatic part was freed from sulfur compounds by further adsorption. The narrow fractions obtained by fractionation contained a limited number of individual hydrocarbons and were analyzed mostly by the refractive index and refractive-intercept methods. The paraffins and naphthenes up to this point were separated from fractions boiling up to 102°C and the aromatics up to 160°C. The results are summarized in Table 72.

Gooding *et al.*^{33b} determined individual hydrocarbons in the fraction boiling from 97 to 243°F (36 to 117°C) for various crudes. The method used was similar to that of the Bureau of Standards: fractional distillation (of the whole gasoline, however) and determination of individual hydrocarbons in narrow fractions by specific dispersion (aromatics) and refractive intercept (naphthenes and paraffins). In view of variation of the refractive intercept for homologs (Chapter 2), graphical analysis charts (refractive intercept vs. density) have been developed for each fraction on the basis of the data available for individual hydrocarbons

boiling in the range of the fraction. The accuracy of the paraffin or naphthene content has been estimated as 10 per cent. The results are summarized in an abbreviated form in Table 72a.

In connection with the toluene problem, Fischer and Welty^{27a} determined the content of toluene and methylcyclohexane (easily convertible into toluene) in the following crude oils:

Crude oil	Per cent by volume of—	
	Toluene	Methylcyclohexane (+ ethylcyclopentane up to 15-20%)
Texas coastal	0.03	1.2
Conroe, Texas	2.0	2.5
East Texas	0.40	1.7
Kettleman Hills, Calif.	0.70	2.1
Midway light, Calif.	0.02	0.52
No. Sweden mixture	0.80	3.7
Panhandle, Texas	0.22	2.3
Pecos, Texas	0.03	1.0
Refugio, Texas	0.26	2.9
Salt Flat-Regan, Texas	0.19	1.5
Santa Maria, Calif.	0.14	0.79
Sugarland, Texas	none	2.1
Tomball mixture, Texas	1.1	2.1
Tinsley, Mississippi	0.08	0.65
West Texas	0.50	1.3

The data on the chemical composition of various American, Russian and Rumanian gasolines are given in Tables 73-79. Here also the basic method was fractional distillation, resulting in the separation of individual hydrocarbons or narrow fractions containing a small number of hydrocarbons. The composition of the narrow fractions was determined mostly by refractive index, etc., if the individual hydrocarbons were identified. From the quantitative standpoint, these data are less reliable than those obtained by the Bureau of Standards. The comparison of the composition of a Bradford gasoline, as determined by Tongberg *et al.*¹⁰² and by Forziati *et al.* (Bureau of Standards)²⁹ shows, *e.g.*, a considerable difference in the content of normal paraffins, methyl pentanes, and methylcyclohexane. The figures of Tongberg *et al.* are invariably lower, by approximately 40 per cent (of the content of the hydrocarbon), as compared with those of Forziati *et al.* (the difference in the end point of the gasolines has been accounted for). The data of the Russian authors particularly should be considered as very approximate.¹⁰⁶

The content of low molecular-weight paraffins—butanes and pentanes—in straight-run gasolines is not characteristic, and depends largely upon the conditions of separating the crude oil and gas. On the average, light straight-run gasolines (*i.e.*, those rich in low-boiling fractions) may contain 1 per cent isobutane, 2-3 per cent normal butane, 2 per cent isopentane and 5 per cent normal pentane. In a few straight-run gasolines, however, the content of isopentane is comparatively high, even higher than that of normal isomer. A third isomeric pentane-neopentane has

been found in various straight-run gasolines (E. Texas, W. Texas, Hobbs) but in small quantities averaging 0.03 per cent of the crude by volume.^{43a}

Normal paraffins occur in most gasolines, particularly paraffinic, *i.e.*, Pennsylvania, Ponca City, etc. In the Ponca City 55°-180°C fraction they are about $\frac{1}{3}$ of the fraction. Nevertheless, numerous isomeric paraffins have been isolated. As a rule, slightly branched paraffins predominate over highly branched. Thus monomethylpentanes, monomethylhexanes, etc. have been found in comparatively large amounts. The Michigan straight-run gasolines (Tables 72 and 74) are particularly rich in normal paraffins, which constitute the major part of these gasolines. Gasolines rich in isoparaffins are comparatively rare (Tables 55, 72, 72a).

Cyclohexane, methyl-, dimethyl-, and trimethylcyclohexanes, methyl-, dimethyl-, and trimethylcyclopentanes predominate among the naphthenic hydrocarbons present in gasolines. Cyclopentane is represented in a minute amount. Naphthenic hydrocarbons with another number of carbon atoms in the ring than 5 or 6 so far have not been detected in gasolines, and their presence, at least in any appreciable amount, seems improbable. Markownikoff⁷⁷ suspected the presence of cycloheptane, or suberane, in the fraction of Baku gasoline boiling between 117° and 118°C. Leslie and White⁶⁰ found the same hydrocarbon in the 117°-122°C fraction of Ponca City gasoline. The cycloheptane structure of these hydrocarbons, however, cannot be considered as proved.

The presence of naphthenes with three or four carbon-atom cyclic structure, as well as of naphthenes with a bridge in the ring, seems unlikely in view of the absence of optic exaltation in straight-run gasolines and their fractions free of aromatics.

The aromatic hydrocarbons are represented by all known hydrocarbons boiling in the range of gasolines. The content of benzene is usually small, and other benzene homologs are present in larger amounts.

Table 80 summarizes the data on the distribution of typical hydrocarbons in paraffinic gasolines, *i.e.*, from paraffin and mixed-base crude oils. The close similarity in the chemical composition of paraffinic straight-run gasolines is remarkable. Gasolines of this type have about the same composition independently of their geological or geographical origin.

The data on individual hydrocarbons in naphthenic straight-run gasolines are summarized in Table 81. The data of Tables 72, 72a, 77 and 79 show that isoparaffins apparently predominate in naphthenic gasolines. An extreme case is the Yates straight-run gasoline containing only isoparaffins (Table 75). Similar gasolines have been reported for some Trinidad crude oils.⁸²

The difference between paraffinic and naphthenic gasolines is rather quantitative than qualitative. Both types of gasolines contain the same hydrocarbons, normal and iso-paraffins, homologs of cyclopentane, cyclo-

hexane and its homologs, and aromatics, but in different proportions. As will be seen later, high-boiling fractions of crude oils may differ chemically to a much greater extent than low-boiling.

The occurrence and distribution of individual hydrocarbons in straight-run gasolines and crude oils has no correlation with the thermodynamic stability of hydrocarbons. For instance, the predominance of normal paraffins in crude oils does not correspond to the relative instability of such hydrocarbons compared to branched isomers under the low-temperature conditions in which the crude oils were undoubtedly formed. It is known that at temperatures up to at least 200°C the branched paraffins are more stable than corresponding normal hydrocarbons, and largely predominate over normal paraffins under equilibrium conditions.⁹¹

One would not expect, however, any correlation between the composition of crude oils and the thermodynamic stability of hydrocarbons. As a matter of fact, almost all petroleum hydrocarbons and compounds are thermodynamically unstable, and exist only because of the inactivity of the hydrocarbons in question. The free energy of hydrocarbons, compared with carbon, hydrogen and methane, is much greater than, for instance, in any isomerization process. The isomerization of petroleum hydrocarbons, according to the free energy relations at low temperatures (in the absence of specific catalysts), would be just as improbable as the spontaneous decomposition of hydrocarbons into carbon, hydrogen, and methane. By the same reasoning, the absence of olefins and other unsaturates in crude oils is due not to their particular thermodynamic instability but to their activity. Crude oils consist of hydrocarbons and compounds which are thermodynamically unstable but kinematically inactive.

Text cont'd on p. 217

Table 70. Hydrocarbons Isolated from (Depentanized)
Ponca City Straight-run Gasoline.

Hydrocarbon	Boiling Point at 760 mm (°C)	% by Vol of Crude Oil*	Ref
<i>Paraffins</i>			
2,3-Dimethylbutane	58.0	0.06	5
2-Methylpentane	60.4	0.12	5
3-Methylpentane	63.3	0.25	5
<i>n</i> -Hexane	68.7	0.7	6
2,2-Dimethylpentane	78.9	0.04	9
2-Methylhexane	89.7	0.35	33
3-Methylhexane	92.0	0.2	37
<i>n</i> -Heptane	98.4	1.1	37
2-Methylheptane	117.2	0.5	56
<i>n</i> -Octane	125.4	1.0	59
2,6-Dimethylheptane	135.2	0.1	119, 121
Isononane (probably 2,3-Dimethylheptane)	140.7	0.05	112
4-Methyloctane	142.4	0.06	110
2-Methyloctane	143.3	0.2	110
3-Methyloctane	144.2	0.06	110
<i>n</i> -Nonane	150.7	1.0	60, 104
<i>n</i> -Decane	174.0	0.8	8, 60

*The actual percentage may be 1–1½ times greater than the below figures.

Table 70. Hydrocarbons Isolated from (Depentanized)
Ponca City Straight-run Gasoline. (Continued)

Hydrocarbon	Boiling Point at 760 mm (°C)	% by Vol of Crude Oil	Ref
<i>Naphthenes</i>			
Methylcyclopentane	71.8	0.25	36
Cyclohexane	80.8	0.35	7
1,1-Dimethylcyclopentane	87.5	0.05	10
<i>trans</i> -1,3-Dimethylcyclopentane	90.9	0.2	33
<i>trans</i> -1,2-Dimethylcyclopentane	91.9	0.3	83
Methylcyclohexane	100.8	0.3	37
<i>trans</i> -1,3-Dimethylcyclohexane	121.0	0.15	55
Ethylcyclohexane	131.8	0.1	88
Nononaphthene (probably cyclopentane structure)	136.7	0.1	118
1,2,4-Trimethylcyclohexane	141.2	0.1	112
<i>Aromatics</i>			
Benzene	80.2	0.08	6
Toluene	110.5	0.3	11
Ethylbenzene	136.1	0.03	117
<i>p</i> -Xylene	138.4	0.04	116
<i>m</i> -Xylene	139.2	0.12	116
<i>o</i> -Xylene	144.4	0.22	116
Isopropylbenzene	152.4	0.03	120
1,3,5-Trimethylbenzene (mesitylene)	164.6	0.02	69
1,2,4-Trimethylbenzene (pseudocumene)	169.2	0.2	69
1,2,3-Trimethylbenzene (hemimellitene)	176.1	0.06	69

Table 71. Hydrocarbons Suspected in (Depentanized)
Ponca City Straight-run Gasoline.^{57, 59, 88a}

Hydrocarbon	Boiling Point at 760 mm (°C)
<i>Paraffins</i>	
2,2,3,3-Tetramethylbutane	106.8
2,5-Dimethylhexane	109.2
2,4-Dimethylhexane	109.9
2,2,3-Trimethylpentane	110.8
3,4-Dimethylhexane	116.5
3-Methylheptane	117.6
4-Methylheptane	118.0
2,2,5-Trimethylhexane	126
<i>Naphthenes</i>	
1,3-Dimethylcyclopentane	90.7
1,2-Dimethylcyclopentane	91.8
Ethylcyclopentane	103.0
1,2,4-Trimethylcyclopentane	112.5-113
Cycloheptane	118.1
1,4-Dimethylcyclohexane	121.7
1-Methyl-2-ethylcyclopentane	124.0
1,2-Dimethylcyclohexane	128.0
<i>n</i> -Propylcyclopentane	131.3
1,3,5-Trimethylcyclohexane	137-139
1,2,4-Trimethylcyclohexane	143-144
<i>Aromatics</i>	
<i>n</i> -Propylbenzene	159.5
1-Methyl-4-ethylbenzene	162.4
1-Methyl-3-ethylbenzene	160.0
1-Methyl-2-ethylbenzene	164.9

Table 72. Hydrocarbons in Straight-run Gasolines, U. S. A.*
Boiling Range 40° to 180°C

Hydrocarbon	Per Cent by Vol						
	Ponca, Okla.	East Texas	Bradford, Penn.	Green- dale, Mich.	Winkler, Texas	Midway, Calif.	Conroe, Texas
Cyclopentane	0.15	0.31	0.23	0.26	0.31	0.79	0.27
2,2-Dimethylbutane	0.12	0.19	0.16	0.05	0.24	0.27	0.20
2,3-Dimethylbutane	0.25	0.46	0.47	0.32	0.55	0.33	0.33
2-Methylpentane	1.24	2.67	3.73	1.44	1.76	1.83	1.61
3-Methylpentane	1.15	2.03	2.22	0.95	4.40	1.24	1.12
<i>n</i> -Hexane	5.98	5.34	6.31	12.11	1.19	2.04	2.48
Methylcyclopentane	2.88	4.03	1.50	1.68	1.63	4.33	2.97
2,2- and 2,4-Dimethyl- pentane	0.31	1.01	0.94	0.32	0.87	0.49	0.42
Cyclohexane	2.36	2.04	1.95	2.14	0.64	2.69	4.34
1,1-Dimethylcyclopentane	0.54	0.61	0.58	0.39	0.65	0.62	0.45
2,3-Dimethylpentane and 2-Methylhexane	3.58	3.91	4.00	2.03	4.70	2.33	2.48
<i>trans</i> -1,3-Dimethylcyclo- pentane	3.94	4.34	1.64	0.73	1.62	5.66	1.56
<i>trans</i> -1,2-Dimethylcyclo- pentane	1.35	1.74	1.54	0.26	1.25	2.21	0.41
3-Methylhexane	1.09	1.29	1.65	0.39	3.87	0.65	0.47
<i>n</i> -Heptane	7.55	5.14	7.71	14.19	1.34	1.28	3.47
Methylcyclohexane	5.39	7.30	6.27	4.42	1.55	6.47	10.10
Benzene	0.46	0.21	0.19	0.63	0.13	0.20	1.23
Toluene	1.53	1.73	1.52	1.77	0.26	1.28	7.37
Ethylbenzene	0.56	0.68	0.26	0.36	0.23	0.66	0.93
<i>p</i> -Xylene	0.29	0.50	0.50	0.28	0.36	0.44	1.78
<i>m</i> -Xylene	1.53	1.93	1.83	1.20	0.24	1.08	6.10
<i>o</i> -Xylene	0.80	0.88	0.63	0.52	0.09	0.63	2.04
Isopropylbenzene	0.21	0.16	0.10	0.13	0.30	0.26	0.32
<i>n</i> -Propylbenzene	0.24	0.23	0.16	0.14	0.20	0.21	0.42

Method of determination: fractionation.^{2a}Table 72a. Hydrocarbons in Straight-run Gasolines, U. S. A.
Boiling Range 97-243°F.

Hydrocarbon	Per cent by volume									
	Coalinga	Conroe	Hast- ings	Jen- nings	Old Ocean	Saxet	Segno	Tom O'Connor	Wade City	Yates Taylor Link
2- and 3-Methyl- pentane	4.45	4.98	3.97	4.50	8.59	2.21	5.93	7.23	2.66	17.68
<i>n</i> -Hexane	7.75	6.44	5.18	9.15	.18	2.20	8.84	7.76	2.04	4.97
Methylcyclo- pentane	10.29	6.51	7.52	5.01	5.42	5.52	6.40	6.70	7.39	3.82
Benzene	2.22	3.27	0.16	3.61	2.28	0	1.82	0.58	0.38	0
Cyclohexane	7.63	10.40	13.66	7.13	7.30	15.07	9.04	10.44	13.89	4.01
2,3-Dimethyl- pentane and 3-Methylhexane	2.69	3.45	4.53	6.14	6.71	2.39	5.32	5.79	2.27	16.28
<i>n</i> -Heptane	5.94	6.90	2.43	8.42	10.92	1.09	7.96	4.96	0.86	2.28
Methylcyclo- hexane	14.55	22.00	32.39	18.07	17.20	37.48	21.58	23.02	35.02	9.52
Toluene	7.94	16.19	0.77	12.02	5.87	0	9.61	3.39	2.64	0

*Method of determination: fractionation.^{2ab}Table 73. Hydrocarbons Isolated from Bradford Straight-run Gasoline,
End Point 400°F.¹⁰²

Hydrocarbon	Boiling Point (°C)	Percentage
2,3-Dimethylbutane	58.0	0.4
2-Methylpentane	60.4	2.2
3-Methylpentane	63.3	0.65
<i>n</i> -Hexane	68.7	3.3
<i>n</i> -Heptane	98.4	4.0
Methylcyclohexane	100.8	3.7
<i>n</i> -Octane	125.4	3.9

Table 74. Hydrocarbons Isolated from Michigan Straight-run Naphthas.⁵³

Hydrocarbon	Boiling Point (°C)	Percentage
Naphtha, boiling range 44°-134°C		
<i>n</i> -Hexane	68.7	11
<i>n</i> -Heptane	98.4	10
Naphtha, boiling range 157°-206°C		
<i>n</i> -Nonane	150.7	10
<i>n</i> -Decane	174.0	12

Table 75. Hydrocarbons Present in Yates (Pecos, W. Texas) Straight-run Gasoline, Boiling Range 42°-210°C.¹⁰¹

Certain	Suspected	Absence Probable
Cyclopentane	2-Methylpentane	Benzene
Cyclohexane	Methylcyclopentane	<i>n</i> -Heptane
Methylcyclohexane (isolated, 0.8%)	2-Methylhexane	<i>n</i> -Octane
Toluene	Dimethylcyclohexanes	<i>n</i> -Nonane
Ethylcyclohexane (isolated, 1%)		<i>n</i> -Decane

Table 76. Hydrocarbons Detected and Isolated from Turner Valley Straight-run Gasoline, E.P. 174°C.*

Hydrocarbon	% by Vol—	
	in Gasoline†	in Crude Oil
<i>Paraffins</i>		
Isopentane, <i>n</i> -Pentane	0.93	0.38
<i>n</i> -Pentane	1.97	0.79
2,2-Dimethylbutane	0.27	0.11
2,3-Dimethylbutane	0.66	0.27
2-Methylpentane	2.30	0.94
3-Methylpentane	1.37	0.56
<i>n</i> -Hexane	5.86	2.40
2-Methylhexane	2.44	1.0
3-Methylhexane	1.72	0.7
<i>n</i> -Heptane	3.92	1.6
2,3, and 4-Methylheptane	1.22	0.5
<i>n</i> -Octane	2.32	0.8
<i>n</i> -Nonane	1.96	0.95
<i>Naphthenes</i>		
Cyclopentane	0.22	0.09
Methylcyclopentane	2.02	0.82
Cyclohexane	1.86	0.76
Dimethylcyclopentanes	1.83	0.75
Methylcyclohexane and ethylcyclopentane	5.38‡	2.2
Dimethylcyclohexanes	1.96	0.8
Ethylcyclohexane	1.47	0.6
<i>Aromatics</i>		
Benzene	0.78	0.36
Toluene	4.90‡	2.0
Xylenes and ethylbenzene	6.12‡	2.5
Trimethylbenzenes	3.92§	1.6

*Method of determination: fractional distillation and calculation on the basis of refractive indices of narrow fractions, removal of aromatics by sulfuric acid.²²

†Calculated from the data of Donald for Turner Valley crude oil. The data of Watson and Spinks¹⁰⁰ for another Turner Valley crude are close to the Donald's data, with few exceptions.

‡These figures seem to be too high. As a matter of fact, the figures of Watson and Spinks for these hydrocarbons are considerably lower.

§In addition to these carbons, the presence of *n*-decane and *n*-undecane is certain, and that of diethylbenzenes, 1,2,3-trimethylbenzene, *n*-butylbenzene, tetramethylbenzenes, amylbenzenes, *n*-butylcyclohexane, and *sec.* and *tert.*-butylcyclohexane is probable.

Table 77. Hydrocarbons Present in Russian Straight-run Gasolines, End Point 150°C.¹⁰⁸

Hydrocarbon	Approximate Per Cent by Wt		
	Baku	Grozny	Maikop
<i>Paraffins</i>			
Isopentane	0.5	2.1	2.2
<i>n</i> -Pentane	1.6	5.9	4.6
Isohexanes	1.0	4.0	0.1
<i>n</i> -Hexane	3.0	7.6	8.6
Isoheptanes	6.1	4.4	2.8
<i>n</i> -Heptane	3.0	9.9	11.1
Isooctanes	9.6	9.0	5.2
<i>n</i> -Octane	5.6	8.9	7.9
Isononanes	5.4	8.6	4.7
<i>n</i> -Nonane	3.0	6.1	3.5
Paraffins total	38.8	66.5	50.7
<i>Naphthenes</i>			
Cyclopentane	0.2	0.1	0.4
Methylcyclopentane	2.6	2.4	5.4
Cyclohexane	7.0	3.3	2.5
Heptanaphthenes	19.3	10.1	13.3
Octonaphthenes	15.5	6.8	6.9
Nononaphthenes	13.3	5.8	5.3
Naphthenes total	57.9	28.5	33.8
<i>Aromatics</i>			
Benzene	0.2	0.3	2.1
Toluene	1.0	1.5	4.7
Xylenes	2.1	3.2	6.5
Aromatics total	3.3	5.0	13.3

Table 78. Cyclohexane Hydrocarbons Present in Surachany Straight-run Gasoline.*

Cyclohexane
Methylcyclohexane
1,2-Dimethylcyclohexane
1,3-Dimethylcyclohexane (predominant among isomers)
1,4-Dimethylcyclohexane
Ethylcyclohexane
1-Methyl-2-Ethylcyclohexane
1-Methyl-3-Ethylcyclohexane
1,2,4-Trimethylcyclohexane

*Method of determination: catalytic dehydrogenation into aromatics and oxidation of the aromatics into acids.^{4, 44, 45, 86}

Table 79. Hydrocarbons Present in Rumanian Straight-run Gasolines, Boiling Range 50°-150°C.⁸⁴

Hydrocarbon	Approximate Per Cent by Wt		
	Merisor	Bucsan	Gura-Ocnitsei, Aromatic-free
<i>Normal Paraffins</i>			
Hexane	5.4	5.3	3.0
Heptane	4.8	8.3	3.1
Octane	3.2	7.5	
Nonane	1.2	5.5	
Normal paraffins total	14.6	26.6	6.1
<i>Isoparaffins</i>			
Hexanes	5.4	5.1	9.4
Heptanes	6.9	7.7	10.9
Octanes	6.4	9.1	9.6
Nonanes	5.2	8.4	
Isoparaffins total	23.9	30.3	29.9

Table 79. Hydrocarbons Present in Rumanian Straight-run Gasolines, Boiling Range 50°-150°C.⁸⁴ (Continued)

Hydrocarbon	Approximate Per Cent by Wt		
	Merisor	Bucsanı	Gura-Ocnitsei Aromatic-free
<i>Naphthenes</i>			
Cyclopentane	0.4	0.1	0.2
Methylcyclopentane	3.7	2.0	7.1
Cyclohexane	3.5	2.7	9.1
Dimethylcyclopentanes	6.0	2.7	10.8
Methylcyclohexane	9.3	7.3	20.4
Naphthene fraction 104°-113°	3.6	1.2	4.9
Dimethylcyclohexanes	11.0	5.7	11.6
Naphthene fraction 126°-150°	16.1	8.4	
Naphthenes total	53.6	30.1	64.1
<i>Aromatics</i>			
Benzene	1.7	2.0	
Toluene	2.1	3.6	
Ethylbenzene and Xylenes	4.1	6.5	
Aromatics total	7.9	12.1	

Table 80. Typical Hydrocarbons of Paraffinic Straight-run Gasolines, in Per Cent by Weight.

Hydrocarbon	Ponca City E.P. 180°	Michigan E.P. 180°	Bradford E.P. 180°	Grozny E.P. 150°	Maikop E.P. 150°	Bucsanı E.P. 150°
<i>n</i> -Hexane	6	12	6	8	9	5
<i>n</i> -Heptane	7	14	8	10	11	8
<i>n</i> -Octane	7		4	9	8	8
<i>n</i> -Nonane				6	4	6
Methylpentanes	2	2	6			
Methylhexanes	4	2	6			
Cyclopentane	0.1	0.3	0.2	0.1	0.4	0.1
Methylcyclopentane	3	2	2	2	5	2
Cyclohexane	2	2	2	3	3	3
Methylcyclohexane	5	4	6			
Benzene	0.5	0.6	0.2	0.3	2	2
Toluene	1.5	1.8	1.5	1.5	5	4

Table 81. Typical Hydrocarbons of Naphthenic Straight-run Gasolines in Per Cent by Weight.

Hydrocarbon	Midway E.P. 180°	Baku E.P. 150°	Merisor E.P. 150°
<i>n</i> -Hexane	2	3	5
<i>n</i> -Heptane	1	3	5
<i>n</i> -Octane		6	3
<i>n</i> -Nonane		3	1
Cyclopentane	1	0.2	0.4
Methylcyclopentane	4	3	4
Cyclohexane	3	7	4
Methylcyclohexane	7		9
Benzene	0.2	0.2	2
Toluene	1.3	1	2

Hydrocarbons in Straight-run Kerosenes and Gas Oils

Ring Analysis. The chemical composition of straight-run kerosenes and gas oils cannot be determined with sufficient accuracy, particularly for naphthenes and paraffins, as has been discussed in Chapter 2. Olefins

and other unsaturates are practically absent in such distillates, as the very small iodine and bromine numbers, not exceeding 1.0, clearly show. Higher values of the iodine number indicate partial cracking or decomposition during distillation.

The ring analysis of kerosenes and gas oils gives figures which differ widely for paraffinic and naphthenic or asphaltic products (Table 82). The percentage of paraffinic side chains is as high as 70 to 80 per cent in kerosenes and gas oils from paraffin and mixed-base crudes (Pennsylvania and various Mid-Continent crudes). The percentage of rings is small in such distillates, and the average number of rings per molecule varies from 1 to 2. Thus the hydrocarbons of such products are either paraffins or mono- and bi-cyclic naphthenes and aromatics with long paraffinic side chains. On the basis of the data of Table 77 and of molecular weight, the average length of the paraffinic side chains may be as great as C_{10} .

Table 82. Ring Analysis of Straight-run Gas Oils.

	Paraffin-base	Asphaltic Base
Specific Gravity at 15°C	0.840	0.900
Boiling Range (°C)	240-375	240-375
Aniline Point (°C)	80	55
Cetane Number	60	35
Percentage of		
aromatic rings	8	22
naphthenic rings	15	35
paraffinic side chains	77	43
Average No. of rings per molecule	1.5	2.5

The percentage of paraffinic side chains in naphthenic kerosenes and gas oils may be as low as 40. The ring content is correspondingly high. The percentage of naphthenic rings is usually much greater than that of aromatic rings. The average number of rings per molecule is from 2 to 3. Thus polycyclic hydrocarbons predominate in such distillates; they are mostly bicyclic and tricyclic naphthenes and aromatics with short paraffinic side chains. The average length of the chains does not exceed C_5 .

As stated in Chapter 3, the percentage of paraffinic side chains includes paraffin hydrocarbons. The content of paraffin hydrocarbons in kerosenes and gas oils, approximately evaluated, may vary in a broad range from such high figures as 40-50 per cent for paraffinic gas oils to 0-10 per cent for highly naphthenic or asphaltic gas oils.

The chemical composition of kerosenes and gas oils is closely related to their technological properties. The kerosenes and gas oils, rich in paraffins and paraffinic side chains, have good burning properties and are excellent Diesel fuels. According to Kreulen,⁴⁹ the cetene number of a gas oil can be calculated on the basis of the chemical composition:

$$\text{Cetene number} = -0.2A + 0.1N + 0.85P,$$

where A , N and P represent respectively the percentage of aromatic rings, naphthenic rings and paraffinic side chains determined by ring

analysis. Cetane numbers are approximately 15 per cent lower than cetene numbers.

The properties of various gas oils in the boiling range from 500°F (260°C) to 720°F (382°C) may be represented as follows:

Origin	Percentage of			Specif. Gravity	Aniline Point (°C)	Pour Point (°C)	Cetane No.
	Arom. Rings	Naphth. Rings	Paraff. Side Chains				
Pennsylvania	7	19	74	0.835	88	15	55
Oklahoma City	10	23	67	0.845	80	15	50
East Texas	12	25	63	0.848	75	15	50
Gulf Coast	15	32	53	0.870	65	-40	40
California	22	35	43	0.890	55	-40	33

Aromatic Hydrocarbons in Kerosenes and Gas Oils

The figures for the content of aromatic hydrocarbons determined by the methods described in Chapters 2 and 3 are fairly reliable for kerosenes and gas oils and are given in Tables 83-86. The content of aromatics in kerosenes and gas oils varies from 10 to 40 per cent for most crudes. It is interesting to note that many highly asphaltic and naphthenic crudes produce kerosenes and gas oils with a moderate content of aromatics (Hould, Kaluga, etc.), as has been also observed for gasolines. The high specific gravity of such kerosenes and gas oils is due to their high content of polycyclic naphthenes. The exceptionally high content of aromatics (about 50 per cent) in kerosenes and gas oils (Perm crude) is an unusual phenomenon.

The data on the content of aromatics given in Tables 83-86 are in good agreement with the data of ring analysis (Table 82). Calculation of the content of aromatics from the percentage of aromatic rings and the average length of paraffinic side chains will give between 15 and 40 per cent—in other words, close to the data of Tables 83-86.

The content of naphthenes and paraffins cannot be calculated on the basis of physical properties of dearomatized kerosenes and gas oils in view of the presence of polycyclic naphthenes and aromatics (Chapters 2 and 3). However, it can be computed that kerosenes and gas oils from paraffin-base and mixed-base crudes contain a large proportion of paraffins. The same distillates from naphthenic and asphaltic crudes are predominantly naphthenic. Heavy high-boiling gas-oil fractions of such crudes may consist almost exclusively of naphthenes and aromatics, the content of paraffins being negligible. Accordingly, the high proportion of aromatic and naphthenic rings in these gas oils (exceeding 55 per cent, Table 82) confirms the fact that the paraffinic side chains present are barely sufficient for combination with the rings.

The aromatics of kerosenes and gas oils can be extracted by such solvents as sulfur dioxide. The treated oils have better burning properties and higher cetane numbers than the original distillates. The treatment of kerosenes high in aromatics is being largely used in refineries.

Table 83. Content of Aromatics in U. S. Straight-run Kerosene Fractions.*

Boiling Range (°C)	Specific Gravity at 15°C	Percentage of Aromatics by Weight
Tonkawa, Oklahoma, sp gr 0.821		
200-250	0.812	22
250-300	0.835	25
Davenport, Oklahoma, sp gr 0.796		
200-250	0.811	17
250-300	0.824	17
Mexia, Texas, sp gr 0.845		
200-250	0.799	12
250-300	0.815	12
Hould, Texas, sp gr 0.936		
200-250	0.859	11
250-300	0.884	20
Huntington Beach, California, sp gr 0.897		
200-250	0.829	25
250-300	0.847	29

*Method of determination: treatment with sulfuric acid and measuring aniline points.⁸³Table 84. Content of Aromatics in Mexican Straight-run Kerosene Fractions.⁷⁹

Crude Oil	Specific Gravity at 60°/60°F	Boiling Range (°C)	Percentage of Aromatics by Weight
Altamira	0.815	163-294	28.3
San Marcos	0.848	172-291	40.4
Juan Casiano	0.800	178-267	22.0
Portero	0.807	171-292	19.2
Zakamixtle	0.799	182-248	20.6
Mecatepec	0.804	181-279	19.5
Furbero	0.814	171-297	22.9
Teapa	0.789	182-268	11.8
Tecnanapa	0.803	153-279	19.5

Table 85. Content of Aromatics in Asiatic Kerosenes, Boiling Range 150'

Crude Oil	Specific Gravity	Per Cent by Volume
Koetei (Assam)	0.896	22
"	0.872	46
"	0.853	38
Tarakan (Borneo)	—	32
Miri (Borneo)	—	25

*Method of determination: treatment with 100% sulfuric acid.⁴⁶

Table 86. Content of Aromatics in Russian Straight-run Kerosene and Gas Oil Fractions.*

Boiling Range	Specific Gravity at 15°C	Percentage of Aromatics by Weight
Surachany, Baku, sp gr 0.848		
200-250	0.829	18
250-300	0.836	16
300-350	0.843	16
350-400	0.850	15

Table 86. Content of Aromatics in Russian Straight-run Kerosene and Gas Oil Fractions.* (Continued)

Boiling Range	Specific Gravity at 15°C	Percentage of Aromatics by Weight
Balachany, Baku, sp gr 0.876		
200-250	0.848	19
250-300	0.868	21
300-350	0.881	22
350-400	0.898	24
Bibi-Eibat, Baku, sp gr 0.855		
200-250	0.849	22
250-300	0.870	27
300-350	0.874	28
350-400	0.888	27
New Oilfield, Grozny, sp gr 844		
200-250	0.804	18
250-300	0.830	17
300-350	0.836	14
350-400	0.846	14
Old Oilfield, Grozny, sp gr 0.887		
200-250	0.842	26
250-300	0.876	33
300-350	0.886	33
350-400	0.900	34
Dossor, Emba, sp gr 0.862		
200-250	0.836	9
250-300	0.858	13
300-350		
350-400	0.881	16
Kaluga, Caucasus, sp gr 0.955		
200-250	0.851	1
250-300	0.879	15
300-350	0.899	16
350-400	0.916	23
Perm, Ural, sp gr 0.941		
200-250	0.816	53
250-300	0.876	56
300-350	0.916	64
350-400	0.962	70

*Method of determination: treatment with sulfuric acid and measuring aniline points.⁸⁴

Individual Hydrocarbons in Straight-run Kerosenes

Few individual hydrocarbons are separated from low-boiling fractions of kerosenes and gas oils. Mair and Streiff⁷¹ isolated normal dodecane, naphthalene and both methylnaphthalenes from the Ponca City kerosene fraction (200°-230°C, Table 87). The high proportion of normal dodecane and other normal paraffins seems to be significant for fractions produced from paraffin- and mixed-base crudes. In a later communication the same authors⁷² reported on the isolation of 1,2,3,4-tetramethylbenzene and both methyltetralins from the above Ponca City fraction (Table 87). Hufferd and Kranz⁴⁰ fractionated a Pennsylvania gas oil (including kerosene fractions) boiling between 150° and 350°C with columns of 30-32 theoretical plates. The pressure was reduced after 45

per cent had come over. One per cent fractions were collected, and refractive indices and melting points were determined for each fraction. Every possible normal paraffin occurs in the kerosene and gas-oil fractions, as is manifested by minima in refractive index and corresponding maxima in melting point.

The presence of naphthalene and particularly methylnaphthalenes in kerosene fractions is apparently quite common in various crudes. Mabery and Hudson,⁶⁶ for instance, found naphthalene in a California crude; Jones and Wootton⁴² found naphthalene and methylnaphthalenes in a Borneo petroleum; Birch and Norris³ in a Persian kerosene; Tasaki and Yamamoto⁹⁹ in a Japanese crude; and Cosciug¹⁷ in Roumanian crudes. In addition to naphthalene and methylnaphthalenes, the last author found 2,6-dimethylnaphthalene, other isomeric dimethylnaphthalenes, and isomers of trimethylnaphthalene.

Garat and Irimescu⁸¹ isolated 2,3,6-trimethyl- and 1,3,6-trimethylnaphthalene from fraction 101-111°C (1.5 mm mercury) and phenanthrene from a higher fraction of a Roumanian crude oil.

The homologs of tetralin and decalin seem to be largely represented in straight-run kerosenes and gas oils, although only tetralin and methyltetralins have so far been actually separated.

Table 87. Hydrocarbons Isolated from Ponca City Straight-run Kerosene Fraction, 200°-230°C Cut.*

Hydrocarbon	Boiling Point (°C at 1 atm)	Percentage by Weight	
		in Fraction	in Crude Oil
<i>n</i> -Dodecane	216.26	13.6 ± 0.8	1.0
1,2,3,4-Tetramethylbenzene	205.4	1.06 ± 0.07	0.078
Tetralin	207.57	0.27 ± 0.03	0.020
1-Methyltetralin	234.35	0.65 ± 0.12	0.048
2-Methyltetralin	224.03	0.68 ± 0.06	0.050
Naphthalene	217.96	0.46 ± 0.04	0.034
1-Methylnaphthalene	244.78	0.84 ± 0.06	0.062
2-Methylnaphthalene	241.14	1.80 ± 0.10	0.132
Total		19.4 ± 0.8	1.4

*Method of determination: fractionation by distillation and crystallization, solvent treatment and other physical and chemical methods.^{71, 72}

Thus, paraffins and derivatives of monocyclic and condensed bicyclic naphthenes and aromatics are unquestionably the main constituents of kerosenes and gas oils. As has been stated above, paraffins may be absent in high-boiling gas oils from naphthenic crude oils. Condensed tricyclic naphthenes and aromatics may also be present in high-boiling fractions of gas oils; these compounds will be discussed later in connection with the hydrocarbons of lubricating oils.

The question of the presence of the derivatives of diphenyl and dicyclohexyl, as well as of diphenylmethane or triphenylmethane, is not at all clear. Grosse and Mavity³⁴ dehydrogenated a solvent extract from a kerosene fraction (200°-250°C) of Placedo crude over a chromium oxide catalyst and claimed that a substantial quantity of diphenyl, as well as of dimethylnaphthalenes, was isolated from the products of dehydrogenation. These hydrocarbons are considered to be a result of

dehydrogenation of the dicyclohexyl and dimethyldecahydronaphthalenes present in the virgin kerosene fraction.

It is certain, however, that the derivatives of condensed aromatics and naphthenes, such as naphthalene, phenanthrene, etc., or hydrogenated naphthalene and similar hydrocarbons, at least predominate in straight-run kerosenes and gas oils.

LUBRICATING OILS

Ring Analysis of Lubricating Oils

In view of the absence of unsaturates in straight-run gasolines and gas oils, the presence of such hydrocarbons in lubricating distillates and oils seems improbable. Nevertheless, such a possibility cannot be denied *a priori*, because some lubricating oils have comparatively high iodine numbers. Brooks and Humphrey⁴ pointed out that "the iodine numbers of refined lubricating oils indicate relatively very large percentage of unsaturated hydrocarbons. . . . An iodine number of 12, in the case of a medium heavy lubricating oil, corresponds roughly to a monoolefin content of 20 per cent."

It should be borne in mind, however, that the addition iodine numbers of lubricating oils are usually very small unless the distillation is accompanied by some decomposition. Sachanen and Virobianz⁹⁴ showed that the addition bromine numbers of lubricating fractions produced in high vacuum from various crude oils varied from 0.2 to 5.0. The highest addition numbers corresponded to unstable high-boiling fractions of asphaltic crude oils, which are appreciably decomposed at temperatures higher than 350°C. The addition numbers were determined by the McJhliney method which gave more or less reliable qualitative results. Thus, it seems probable that the lubricating oil fractions are completely saturated. The number of carbon atoms in hydrocarbons of lubricating oils varies from 20 to 50, depending upon the boiling range and the chemical structure, as will be seen later. The ring analysis gives approximately the same results as for gas oils.

Carnahan¹³ gives the following data for the ring composition of commercial lubricating oils (Table 88). The ring structure of Pennsylvania neutrals and bright stock is practically identical. Mid-Continent neutrals contain a larger proportion of aromatic and naphthenic rings at the expense of paraffinic side chains. Mid-Continent Extra and Western Extra neutrals, produced as a result of heavy solvent refining, contain a small proportion of aromatic rings and a large percentage of naphthenic rings which are not removed by the solvent treatment.

Von Fuchs and Anderson³⁰ give the following data on the chemical composition of lubricating oils solvent-extracted to the same aromatic content (about 4 per cent aromatic rings, Table 89). These data also show that the content of paraffinic side chains and rings is the same in oils SAE 20 and 40 of the same origin.

Fenske *et al.*²⁷ applied the ring analysis method not only to various neutrals but to the narrow fractions of the neutrals. The condensed data of this investigation are given in Table 90. The percentage of paraffinic side chains varies from 80 per cent in lubricating oils from Pennsylvania crudes to 40 per cent in lubricating oils from asphaltic stocks. Naphthenic rings predominate in lubricating oils from paraffin- and mixed-base crudes; in those from naphthenic and asphaltic crudes the percentage of naphthenic and aromatic rings is approximately equal.

The average number of rings per molecule varies from 1.5 for paraffin-base lubricating oils and fractions to 4.5 for asphaltic lubricating oils. Thus, polycyclic naphthenes and aromatics predominate in lubricating oils, particularly naphthenic and asphaltic.

The average length of paraffinic side chains also depends upon the origin of the lubricating oil, as well as upon the viscosity and the boiling range; it varies from C_7 for asphaltic oils to C_{20} or more for viscous paraffin-base and mixed-base products.

The data of Table 90 show that the narrow fractions of lubricating oils produced by fractional distillation have approximately the same chemical composition expressed in terms of ring analysis, or about the same distribution of aromatic and naphthenic hydrocarbons in each fraction. A certain accumulation of aromatic rings, however, is noticeable in first fractions; this is due to the lower molecular weights and hence to the higher rate of evaporation of aromatic hydrocarbons (compare page 68).

Fractionation by solvent treatment produces quite different results, effecting the separation of aromatics and naphthenes, as well as of cyclic hydrocarbons with short paraffinic side chains from those with long side chains. Carnahan¹³ fractionated by reflux solvent extraction a Mid-Continent neutral into 20 fractions and residuum. The results are given in Table 91. The properties of various solvent fractions, indicated by ring analysis data, differ very substantially. The first extract fractions consist of polycyclic aromatics with short paraffinic side chains causing negative values of the viscosity index. The middle fractions contain a small proportion of aromatics and a large proportion of naphthenes with moderately long paraffinic side chains. The last fractions and residuum contain no aromatics but only naphthenes with long paraffinic side chains. As a result, the viscosity index exceeds 100.

Varteressian, Fenske and Smith¹⁰⁴ have given comparative data on the fractionation of a Pennsylvania neutral by distillation and solvent fractionation. The condensed data are given in Table 92; they show that fractional solvent extraction produces fractions containing as much as 85 per cent of paraffinic side chains and 15 per cent of naphthenic rings, whereas aromatic rings are absent. The average number of rings per molecule in these fractions is 1.25-1.30, *i.e.*, the fractions consist mostly of monocyclic naphthenes with very long paraffinic side chains, up to

$C_{30}H_{61}$ in this case. The viscosity index of such fractions is much greater than 100.

Hillman and Barnett³⁸ studied the fractions of a straight-run residuum from a California asphalt-base crude oil. The residuum was freed from asphaltenes by treatment with isopentane and then fractionated by the addition of propane into 19 fractions. The ring analysis data for some fractions are as follows:

Fraction	Per Cent of Residuum	Sp Gr at 20°C	-Percentage by Wt of-		
			Aromatic Rings	Naphthenic Rings	Paraffinic Side Chains
19	9.51	0.9075	14	35	51
10	5.80	0.9613	27	24	49
5	2.18	1.0157	45	10	45
1	15.80	1.0479	53	1	46

These data show that the heaviest hydrocarbons of petroleum fractions may be completely aromatic without naphthenic rings. Fractions 5 and 1 undoubtedly contain a large proportion of neutral resins.

The ring structure of lubricating oils predetermines their commercial properties. The specific gravity and refractive index are high for lubricating oils with a large percentage of rings, particularly aromatic. The close relationship between the percentage of rings (or paraffinic side chains) and the viscosity index has been discussed. At the same molecular weight or boiling range, the greater the number of rings the higher the viscosity, particularly at low temperatures, because the viscosity of hydrocarbons increases with increasing number of rings at the same molecular weight (see page 245). As a result, naphthenic or aromatic lubricating oils have a lower boiling range and greater volatility than paraffin-base lubricating oils of the same viscosity. This explains the well known fact that the flash point is higher for the latter than for the former. The properties of paraffin- and asphaltic-base lubricating oils may be summarized as follows:

	Paraffin-base	Asphaltic-base
Molecular weight	350-650	260-450
Percentage of paraffinic side chains	75	45
Percentage of naphthenic aromatic rings	25	55
Average number of rings	1.7	3.5
Specific gravity (60°/60°F)	0.86-0.89	0.91-0.97
Viscosity at 100°F (S.U.)	100-2350	100-7000
Viscosity at 210°F (S.U.)	39-150	37-150
Viscosity Index	100	-30
Flash (°F)	390-550	335-465

The properties of mixed-base lubricating oils lie between those of paraffin- and asphaltic-base oils, but much closer to the former.

It is of interest that such properties of lubricating oils as specific gravity, refractive index, and viscosity, change gradually with increasing boiling range, whereas the percentage of rings and the viscosity index remain practically constant.

Fenske *et al.*²⁶ and Hirschler³⁹ developed correlations of the molecular weight of lubricating oils with the viscosity and viscosity index and with the viscosity and density.

Little can be said about the physical structure of lubricating oils; they are substantially homogeneous mixtures of hydrocarbons and other constituents, which are miscible in all proportions, with the exception of solid paraffins.

The theory of the colloid or "isocolloid" structure of lubricating oils is still frequently discussed and cited, in spite of its inherent improbability. The average molecular weight of lubricating oils varies from 300 to 800, *i.e.*, much below that of colloidal substances, which is of the order of at least 10,000 or more. As will be seen in Chapter 9, even oxygen-containing neutral resins present in lubricating oils have a comparatively moderate molecular weight and form true, non-colloidal solutions with hydrocarbons. Only asphaltenes form colloidal solutions in petroleum oils. The asphaltenes, however, are usually absent in lubricating oils, or may be present in some heavy, improperly refined lubricants in an amount not exceeding a small fraction of one per cent. The phenomena of dispersion do not play any significant part in lubricating oils. Individual hydrocarbons of proper molecular structure may have the same or better lubricating properties than conventional lubricating oils (page 242).

The theory of the colloid structure of lubricating oils originated in the infancy of colloid chemistry, when merely the term "colloid structure" seemed to be an adequate explanation of lubricating properties. The magic of words is frequently longer-lived than might be expected.

Table 88. Ring Analysis of Commercial Lubricating Oils.

Lubricating Oil	Viscosity at 100°F Saybolt	Viscosity Index	Percentage of		
			Aromatic Rings	Naphthenic Rings	Paraffinic Side Chains
Pennsylvania neutral	185.6	101	9	15	76
Pennsylvania neutral	202	97	10	14	76
Pennsylvania bright st	2520	99	9	13	78
Mid-Cont neutral	207	73	11	25	64
Mid-Cont Extra neutral	202	98	5	22	73
Western Extra neutral	171	101	0	31	69

Table 89. Ring Analysis of Lubricating Oils.

	Penna.	Mid-Cont.	W. Texas	California	Gulf
Oil SAE 40					
Gravity (A.P.I.)	29.4	28.8	28.6	23.8	23.0
Sp gr (20°/4°)	0.876	0.881	0.883	0.907	0.912
Viscosity (210°F)	76	71	65	72.6	64.0
Viscosity Index	107	99	86	54	33
Mol Weight	494	450	463	406	378
Rings/molecule	2.0	2.5	2.5	3.0	3.0
Paraffinic side chains (%)	76	71	69	56	53
Naphthenic rings	20	25	26	40	43
Aromatic rings	4	4	5	4	4

Table 89. Ring Analysis of Lubricating Oils. (Continued)

	Penna.	Mid-Cont.	W. Texas	California	Gulf
Oil SAE 20					
Gravity (A.P.I.)		31.4	29.9	26.7	25.4
Sp gr (20°/4°)		0.865	0.873	0.891	0.898
Viscosity (210°F)		45.0	43.9	44.1	43.1
Viscosity Index		92	85	57	33
Mol Weight		358	336	327	311
Rings/molecule		1.8	2.0	2.5	2.5
Paraffinic side chains (%)		71	65	55	52
Naphthenic rings		26	31	41	44
Aromatic rings		3	4	4	4

Table 90. Ring Analysis of Lubricating Oils (Dewaxed):
Composition of Various Neutrals and Their Fractions.

No.	-Saybolt at 210°F	Viscosity- at 100°F	Viscosity Index	Sp Gr (20°/4°)	Aniline Point (°C)	Composition—				Average Rings/ Molecule
						Mole- cular Weight	Arom. Rings	Naphth. Rings	Paraffin Side Chains	
Pennsylvania 180 Neutral										
Neutral	45.50	184.8	100	0.8720	101.1	395	7	18	75	1.6
Fr. 1	36.63	75.87	100	0.8716	84.8	338	13	18	69	1.8
Fr. 12	45.50	184.4	100	0.8699	101.1	393	7	17	76	1.6
Fr. 21	57.94	394.2	97	0.8762	109.6	482	7	15	78	1.8
Resid.	76.64	712.9	97	0.8832	113.2	521	5	20	75	2.2
Rodessa Neutral										
Neutral	45.31	184.5	97	0.8763	98.1	397	9	20	71	1.9
Fr. 4	38.13	93.80	86	0.8878	82.0	329	16	21	63	2.1
Fr. 9	45.24	184.1	96	0.8767	98.9	400	8	20	72	1.9
Fr. 15	51.06	279.9	94	0.8802	103.7	442	7	20	73	2.0
Mid-Continent Neutral										
Neutral	49.37	290.3	67	0.8990	90.2	377	11	24	65	2.2
Fr. 1	36.22	78.1	52	0.9057	66.9	265	15	28	57	1.9
Fr. 10	48.07	272.6	59	0.8977	89.6	381	12	24	64	2.4
Fr. 18	63.80	619.6	68	0.8979	100.1	417	8	22	70	2.2
Resid.	106.3	1807	70	0.9090	105.6	494	8	13	79	1.8
Mid-Continent Neutral										
Neutral	57.98	524.8	51	0.9124	91.6	400	11	29	60	2.7
Fr. 1	35.18	69.87	25	0.9043	65.7	263	12	45	43	2.5
Fr. 9	50.54	360.6	31	0.9101	85.6	378	13	29	58	2.8
Fr. 17	103.9	1920	56	0.9166	102.1	497	10	24	66	2.9
Resid.	140.0	3029	68	0.9167	108.6	571	10	22	68	3.2
Gulf Coast Neutral										
Neutral	51.70	440.2	8	0.9252	78.2					
Fr. 1	36.38	84.42	18	0.9275	57.3	268	19	41	40	2.7
Fr. 10	50.54	408.9	6	0.9204	78.4	355	15	32	53	2.9
Fr. 18	82.32	1872	-21	0.9343	85.4	396	12	38	50	3.5
California Neutral										
Neutral	49.19	381.6	-4	0.9324	68.1	330	20	32	48	2.9
Fr. 3	35.18	71.96	1	0.9162	55.4	254	18	43	39	2.5
Fr. 10	47.11	358.2	-38	0.9374	60.9	313	24	29	47	2.8
Fr. 18	88.75	2687	-66	0.9480	73.0	409	22	33	45	3.9
Resid.	140.1	5528	-17	0.9488	91.6	456	17	42	41	4.6

Table 91. Reflux Extraction of Mid-Continent Neutral.

		Ring Analysis Data, Per Cent of			
Cut	Per Cent	—Viscosity (S.U.) at—		V.I.	Paraffinic Side Chains
		210°F	100°F		
Original oil	100	44.6	207	73	64
1	3.79	52.3	600	-49	48
5	4.73	52.1	576	-40	45
10	4.33	43.3	179.4	78	60
15	4.29	42.0	142.4	105	70
20	3.00	43.4	157.2	115	75
Residuum	8.89	44.7	163.3	124	80

Table 92. Fractionation of Filtered Pennsylvania Neutral by Distillation and Solvent Extraction.

Cut No.	Wt. Per Cent of Charge	—Viscosity at—		Visc. Index	Sp Gr (20°C)	Mol. Weight	Percentage of			Ave. Rings Mol.
		210°F	100°F				Arom. Rings	Naphth. Rings	Paraff. Side Chains	
Fractionation by Distillation										
Original	100	44.8	185.6	101	0.8713	407	9	15	76	1.70
1	2.84	36.3	78.5	92	.8793	308	12	23	65	1.80
12	2.78	40.5	121.8	108	.8653	360	8	15	77	1.50
24	2.46	47.2	229	96	.8736	429	6	16	78	1.60
34	3.30	58.6	426	96	.8779	512	9	14	77	2.00
Bottoms	6.07	72.5	700	95	.8853	581	10	15	75	2.40
Fractionation by Reflux Extraction (Acetone)										
Original	100	44.8	185.6	101	0.8713	407	9	15	76	1.70
1	4.54	54.3	656	-37	.9565	335	44	2	54	2.60
5	4.48	44.9	211	73	.8930	353	17	17	66	2.05
10	4.29	41.3	128	115	.8464	374	0	23	77	1.45
21	3.90	49.3	222	124	.8496	473	0	16	84	1.25
Resid.	5.58	52.4	261	124	.8523	506	0	15	85	1.30

Aromatic Hydrocarbons in Lubricating Oils

The content of aromatic hydrocarbons in lubricating oils and their fractions can be determined by the separation of aromatics with sulfuric acid and on the basis of the aniline points or other physical properties before and after separation (Chapter 3). Table 93 includes the data on the content of aromatics in lubricating-oil fractions of various Russian crude oils, determined by separation with 98 per cent sulfuric acid. Strictly speaking, the figures of Table 93 should be considered as the figures of the content of aromatics which react with 98 per cent sulfuric acid. It has been shown, however, that the actual figures of the aromatic content are very close to those given in Table 93. It is understood that concentrated sulfuric acid reacts not only with pure aromatic hydrocarbons but also with naphtheno-aromatic hydrocarbons containing, for instance, one aromatic ring condensed with one or more naphthenic rings.

Thus, the content of aromatics in untreated lubricating-oil fractions varies from 10 to 40 per cent on the average. The higher figures for high-boiling fractions of a Perm crude oil are exceptional and are not characteristic of other crude oils. The content of aromatics in untreated lubricating distillate stocks from Pennsylvania crude oils is close to 10 per cent and in those from California crude oils it amounts to 30 per cent.

The content of aromatic hydrocarbons (or aromatic rings) in an untreated lubricating stock is closely related to the commercial value of the stock. The aromatic hydrocarbons of lubricating stocks have a low viscosity index (negative) and are unstable toward oxidation, which transforms them into resinous and asphaltic products. Thus, the content of aromatics is an approximate measure of the undesirable constituents to be removed in the process of refining.

The aromatic hydrocarbons of lubricating oils and other petroleum products can be extracted by various solvents and may be recovered by separation from the solvent. The separation of aromatics by this method, however, is not quantitative. The aromatics contain a greater

or lesser proportion of other hydrocarbon constituents, depending upon the conditions of the treatment. In addition, resinous and asphaltic compounds are extracted with the same ease as aromatic hydrocarbons, and form a part of the extract. As will be seen in Chapter 9, the content of such resinous and asphaltic constituents in the extract may vary in a broad range from 10 to 50 or 60 per cent, the former figure for extracts from light distillates, the latter for those from heavy residues. In any case, the extracts from distillates consist mostly of aromatic hydrocarbons; thus their properties are close to those of aromatic hydrocarbons. These properties may be summarized as follows: specific gravity is high, amounting to 1.0; the viscosity is also high, particularly in comparison with the original lubricating-oil distillates, but the viscosity index is very low, mostly negative.

Separation of aromatic hydrocarbons by sulfuric acid is much more selective than solvent extraction, since only aromatics and resinous-asphaltic compounds are removed by this reagent. The drawback to this method is the impossibility of recovering the aromatic hydrocarbons from the sulfonic acids. Nevertheless, the physical properties of aromatics separated with sulfuric acid, such as specific gravity or refractive index, can be calculated for various lubricating-oil fractions from the data determined for the fractions before and after treatment with sulfuric acid.⁹⁴ The calculations were made on the assumption of a linear relationship between the specific gravity (refractive index) and composition (Chapter 2). Table 94 contains the calculated data of specific gravity for aromatic hydrocarbons extracted with sulfuric acid from lubricating-oil fractions of various crudes.

The steady increase in the specific gravity with increasing boiling point or molecular weight shows that the aromatics become more and more polycyclic with increasing molecular weight. Other conclusions on the cyclic structure of aromatics and their paraffinic side chains will be discussed in the following sections.

Table 93. Content of Aromatics in Russian Straight-run Lubricating-oil Fractions.⁹⁴

Viscosity (Saybolt Units at 122°F)	Specific Gravity at 15°C	Max. Aniline Point (°C)	Per Cent Aromatics by Weight
Surachany, Baku, sp gr 0.848			
57	0.867	92.6	12
120	0.879	99.6	9
175	0.890	106.6	10
Balachany, Baku, sp gr 0.876			
65	0.898	83.4	24
140	0.911	91.2	24
560	0.920	99.6	22
Bibi-Eibat, Baku, sp gr 0.855			
62	0.905	79.4	27
135	0.917	86.6	28
385	0.928	94.6	26

Table 93. Content of Aromatics in Russian Straight-run Lubricating-oil Fractions.⁹⁴
(Continued)

Viscosity (Saybolt Units at 122°F)	Specific Gravity at 15°C	Max. Aniline Point (°C)	Per Cent Aromatics by Weight
New Oil Field, Grozny, sp gr 0.844			
54	0.864	93.3	11
80	0.878	98.2	13
175	0.897	103.4	14
Old Oil Field, Grozny, sp gr 0.887			
75	0.915	70.8	37
155	0.929	78.0	39
650	0.943	85.8	39
Dossor, Emba, sp gr 0.862			
62	0.886	88.4	16
110	0.891	97.6	14
220	0.897	106.8	10
Kaluga, North Caucasus, sp gr 0.955			
115	0.934	66.4	31
340	0.946	73.2	36
850	0.952	80.8	37
Perm, sp gr 0.941			
75	0.990	52.8	69
205	1.005	58.6	71
650	1.020	60.2	72

Table 94. Specific Gravity of Aromatic Hydrocarbons Separated with Sulfuric Acid from Fractions of Lubricating Oils.

Boiling Range at 1 atm (°C)	Average Molecule	—Specific Gravity at 15°C— from to	
350-400	C ₁₈	0.947	0.990
400-450	C ₂₁	0.974	1.027
450-500	C ₂₅	0.981	1.055
500-550	C ₃₀	0.983	1.043

Paraffin Hydrocarbons in Lubricating Oils

Paraffin hydrocarbons of normal or slightly branched structure, boiling in the range of lubricating-oil distillates, have high melting points and are only slightly soluble in oils at low and moderate temperatures. The content of such hydrocarbons, composing petroleum wax, may be as high as 10 per cent or more in lubricating distillates from paraffin- and mixed-base crudes. In lubricating-oil distillates from naphthenic or asphaltic crudes the content of normal high-melting paraffins is usually very low (Chapter 6). The paraffin wax can be easily separated by filtration or centrifuging in suitable solvents. The commercial lubricating oils with low pour points are practically free from normal and slightly branched paraffins of comparatively high melting points.

Branched high molecular weight paraffins may have very low melting points and are completely miscible with lubricating oils. As will be seen later (Chapter 6), paraffins are completely miscible with petroleum oils at temperatures above the melting points of paraffins. Thus, the low pour points of commercial lubricating oils do not preclude the pres-

ence of branched paraffins. Table 95 includes the melting points of isomeric tetracosanes.

Table 95. Melting Points of Isomeric Tetracosanes.²³

Hydrocarbon	Melting Point (°C)
<i>n</i> -Tetracosane	51.1
2-Methyltricosane	42
2,2-Dimethyldocosane	34.6
5- <i>n</i> -Butyleicosane	

The data of Table 95 show that the melting point of a high molecular weight paraffin depends greatly upon the degree of branching. Highly branched isomers of tetracosane and similar high molecular weight paraffins are liquid at room temperature and even at lower temperatures. Klos, Neuman-Pilat and Pilat⁴⁷ synthesized 11-decyldocosane, $C_{12}H_{24}$ ($C_{10}H_{21}$)₂. This hydrocarbon is liquid at room temperature and has lubricating properties: boiling point at 1 mm 233°-235°C, $d_{20} = 0.8152$, $n_D = 1.4554$, viscosity at 20°C, 26.53 centipoises (152 Saybolt units) and at 100°C 2.94 centipoises. Recently Cosby and Sutherland⁴⁸ studied thoroughly the effect of the structure of isoparaffins upon their melting points and viscosity. The following isomeric *n*-butyldocosanes were synthesized:

		Melting Point (°C)	Viscosity at 100°F, (centipoises)
11- <i>n</i> -Butyldocosane	$C_{10}-C-C_{11}$ C_4	0.0	10.41
9- <i>n</i> -Butyldocosane	C_8-C-C_{13} C_4	1.3	10.61
7- <i>n</i> -Butyldocosane	C_6-C-C_{15} C_4	3.2	11.10
5- <i>n</i> -Butyldocosane	C_4-C-C_{17} C_4	20.8	11.48
normal hexacosane	$C-C_{24}-C$	57	

These data show clearly that the same paraffinic side chain, in this case C_4 , may have a quite different effect, depending upon its position: the central position of the side chain produces the maximum depressing effect on the melting point, and *vice versa*. Thus, all high molecular weight paraffins containing about 25 carbon atoms, which have at least one paraffinic side chain, C_4 or longer, in the middle of the molecule, are liquid at room temperature. The structure of the side chain also has a pronounced effect upon the melting point, as the following data of the same authors show:

		Melt. Point (°C)	Visc. at 100°F
11- <i>n</i> -Amylheneicosane	$C_{10}-C-C_{10}$ C_5	-9.1	10.08
11-(3-pentyl)-heneicosane	$C_{10}-C-C_{10}$ C_2-C-C_2	glass at -40	10.39

Whitmore, Cosby, Sloatman and Clarke¹²² also found that the heneicosanes substituted in position 11 ($C_{10}H_{21}.CHR.C_{10}H_{21}$) have low melting points (below $-7^{\circ}C$), with the exception of 11-phenyl-heneicosane (mp $20.8^{\circ}C$).

On the basis of these investigations it is obvious that high molecular weight branched paraffins, having a sufficient degree of branching and a centralized position of the side chain are liquid at low temperatures and have lubricating properties.

Kyropoulos⁵² compared the refractive indices and specific gravities of isoparaffins known at that time with those of Pennsylvania lubricating oils and concluded that these oils are composed largely of isoparaffins. Bielenberg² and Vlugter, Waterman and van Westen¹⁰⁷ showed that Kyropoulos' conclusions were erroneous. There is no doubt at present that even the Pennsylvania lubricating oils are composed of cyclic hydrocarbons with long paraffinic side chains, as has been accepted by Mabery. The question of the possible presence of highly branched liquid paraffins in lubricating oils, however, is still open for further discussion, since a certain proportion of liquid isoparaffins to cyclic hydrocarbons seems to be at least not improbable.

Mair and Willingham⁷³ pointed out that none of the narrow wax-free lubricating fractions, produced from a Ponca City crude oil and treated with solvents, was observed to be richer in hydrogen than C_nH_{2n} , corresponding to monocyclic naphthenes. Any fraction consisting of bicyclic naphthenes and isoparaffins of the composition C_nH_{2n} should be easily separated by solvent treatment into a paraffinic raffinate and a naphthenic extract. Thus the authors came to the conclusion that "no appreciable percentage of isoparaffins exists in these fractions."

An extensive investigation along this line was made by Müller and Neyman-Pilat.⁸³ Isoparaffins to be present in lubricating oils were separated by repeated extractions with various solvents. The final raffinate produced in a very small yield with respect to the original oil would contain at least a considerable proportion of isoparaffins, if those were present in the oil. A Polish bright stock (from Schodnica, sp gr 0.948 and molecular weight 535) was extracted four times with benzene-liquid sulfur dioxide, then four times with nitrobenzene, then twice with furfural and finally 24 times with pyridine. The last raffinate, obtained in a yield of 0.41 per cent of the original oil, was not paraffinic, corresponding to $C_nH_{2n-0.8}$.

Three Pennsylvania lubricating oils of specific gravity 0.905 (molecular weight 657), 0.8748 (molecular weight 466) and 0.8685 (molecular weight 400) were treated with solvents in a similar manner. The final raffinate was crystallized in ethyl ether at $-70^{\circ}C$. The crystallized raffinates were obtained in yields of 2.72, 1.2 and 7.5 per cent, respectively, and had the following formulas: $C_nH_{2n-0.4}$, $C_nH_{2n+0.4}$ and $C_nH_{2n+0.4}$. The last two raffinates may contain as much as 35 per cent isoparaffins, if the naphthenes are monocyclic, or more, if they are not.

Thus only the light Pennsylvania lubricating oil of specific gravity 0.8685 may contain as much as about 3 per cent isoparaffins. In other Pennsylvania lubricating oils investigated, as well as in the naphthenic bright stock, the content of isoparaffins is negligible.

In addition to this, it should be pointed out that the fractions produced after the repeated extractions should contain also a certain proportion of normal paraffins which were not removed in the process of dewaxing. Therefore, the content of isoparaffins should be correspondingly less. The pour point of the raffinates $C_nH_{2n+0.4}$ was above $+10^\circ C$, indicating the possible presence of normal paraffins.

Thus it seems to be fairly safe to conclude that lubricating oils of low pour point (produced directly from naphthenic crude oils or, after dewaxing, from paraffinic crude oils) are composed almost entirely of cyclic naphthenic and aromatic hydrocarbons, the percentage of isoparaffins in such oils either being negligible or not exceeding a few per cent in some cases. It is understood that lubricating oils may contain, in addition to hydrocarbons, a certain proportion of resinous sulfur and oxygen compounds, which have also a cyclic structure (Chapter 9).

Rings of Lubricating-oil Hydrocarbons

Very little is known of the structure of rings forming the cyclic hydrocarbons of lubricating oils. The analogy between low-boiling fractions and lubricating oils leads to the conclusion that the derivatives of benzene, cyclohexane, cyclopentane, naphthalene, hydrogenated naphthalenes and tricyclic aromatic and hydroaromatic hydrocarbons may be present in lubricating oils.

Mabery⁶⁷ was the first to recognize the cyclic structure of lubricating oils on the basis of empiric formulas and the saturated character of lubricating oils.

Separation of the aromatic hydrocarbons present in dewaxed lubricating oils leaves naphthenic hydrocarbons, the empiric formula of which may give a clearer indication of the ring structure of hydrocarbons than does the empiric formula of total oils. Mabery, Buck, Zoule, Coats and Best^{15, 62, 63, 64, 65, 67} determined the empiric formulas of the naphthenes produced from lubricating oils of various origins, and found that they varied from C_nH_{2n-2} to C_nH_{2n-8} . Bestougeff¹⁴ investigated the naphthenes of Russian lubricating fractions and gave formulas varying from C_nH_{2n-2} to C_nH_{2n-6} . For the aromatic hydrocarbons separated either by solvent or by sulfuric acid, the authors cited found the formulas from C_nH_{2n-8} to C_nH_{2n-44} .

Later Davis and McAllister,¹⁹ Waterman *et al.*¹⁰⁸ and others showed that the average number of rings per molecule can be determined under certain assumptions (Chapter 3). It corresponds to the average number of rings in cyclic molecules of low-pour point lubricating oils due to the fact that such oils consist almost entirely of cyclic hydrocarbons, as has been discussed above.

Tables 89, 90, and 92 give the data on the average number of rings in cyclic hydrocarbons of some lubricating oils, calculated by the Waterman method on the assumption that the rings are of the six-carbon atom structure.

The most illuminating conclusions on the ring structure of lubricating oils were reported by Rossini,⁹⁰ Leslie and Heuer,⁵⁸ and Mair, Willingham and Streiff,⁷⁴⁻⁷⁶ as a result of extensive investigations of a lubricating stock from a Ponca City crude. The lubricating stock was produced from the crude in the amount of 10 per cent and was dewaxed at -18° in ethylene chloride. The wax-free portion was subjected to extraction at 40° with liquid sulfur dioxide. The raffinate was treated with silica gel to produce a "water-white" oil and a portion was adsorbed by silica gel. The extract in liquid sulfur dioxide was treated with petroleum ether at -55° to extract a "petroleum-ether soluble" portion, an asphaltic portion remaining in the sulfur dioxide solution. The "petroleum-ether soluble" portion was combined with the previous portion adsorbed by silica gel to produce the "extract" portion of the lubricating stock. Thus, the following fractions were separated:

(1) The "wax" portion, 35 per cent.

(2) The "asphaltic" portion, 8 per cent.

(3) The "extract" portion, 22 per cent, boiling range at 1 mm from 170° to 290° , viscosity of fractions from 100 to 9000 Saybolt units at 100°F , viscosity index from -80 to -150 , density 0.98, refractive index 1.56, and specific dispersion 0.0195.

(4) The "water-white" portion, 35 per cent, boiling range at 1 mm from 190° to 270° , viscosity of fractions from 100 to 500 Saybolt units at 100°F , viscosity index from 90 to 110, density (at 25°) from 0.86 to 0.89, refractive index (25°) from 1.47 to 1.49, specific dispersion 0.0102.

Only the "water-white" and "extract" portions were investigated. Both portions were fractionated by distillation and extraction.⁷⁰ Each portion was first fractionated by distillation in high vacuum to produce a large number of substantially constant-boiling fractions. The fractions obtained were then fractionated by extraction to produce final "homogeneous" fractions. Acetone (plus some water for more soluble fractions) was used as a solvent for the "white-water" fractions and methyl cyanide (plus some acetone for less soluble fractions) for the "extract" fractions. Each "final" homogeneous fraction, representing $\frac{1}{40,000}$ part of the original crude oil, consisted of compounds of substantially similar molecular size and type.

The fractions of the "water-white" portion contained no sulfur, oxygen or nitrogen, whereas those of the "extract" portion contained, on the average, about 0.9 per cent sulfur, 0.1 per cent nitrogen and 0.5 per cent oxygen.

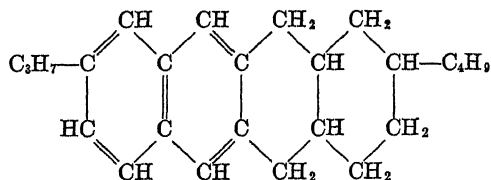
The most important data for the following calculations and computations are: carbon content, hydrogen content, molecular weight, density, refractive index, specific dispersion, boiling point, aniline point, and vis-

cosities at 100° and 210°F. These data were determined for the "water-white" and "extract" portions. The latter were completely hydrogenated (until the specific dispersion reached 0.0100) and the same data were obtained for the hydrogenated fractions. The value of specific refraction or specific dispersion versus molecular weight will give important conclusions as to the number of aromatic and naphthenic rings in the molecule. For instance, the value of 0.0100 for specific dispersion shows that the hydrocarbons are purely naphthenic and that aromatic rings are absent. Another example: the value for specific dispersion of about 0.0130 for 20 carbon atoms shows that the hydrocarbons belong to the derivatives of either benzene or tetraline. The value of specific refraction for a certain number of carbon atoms depends upon the number of rings in the molecule. The increase in hydrogen content (or in the number of hydrogen atoms per molecule) after hydrogenation will give the number of aromatic rings in the virgin molecule before hydrogenation.

It has been postulated in all calculations that the naphthenic rings are of the six-carbon type, and that the rings in aromatic and naphthenic hydrocarbons are condensed by joining through two carbon atoms. The most important results obtained concern the number of aromatic and naphthenic rings in molecules of lubricating oils from 1 to 4 *in toto*, and the combination of aromatic with naphthenic rings in one molecule. The aromatic rings, at least in lubricating oils of Mid-Continent origin, are combined with naphthenic-producing aromatic-naphthenic hydrocarbons which contain 1 naphthenic ring + 1 aromatic ring (derivatives of tetralin), 2 naphthenic + 1 aromatic, 3 naphthenic + 1 aromatic, 2 naphthenic + 2 aromatic, or 1 naphthenic + 3 aromatic.

Another alternative—that the hydrocarbons in question consist of mixtures of aromatic and naphthenic hydrocarbons in suitable proportions—is ruled out. The aromatic and naphthenic hydrocarbons of the "homogeneous" fractions would have different boiling points and different solubilities in the solvent used, and would be easily separated in the operations of fractionation and solvent refining described above.

Rossini, for instance, gives the following formula for an "extract" homogeneous fraction of specific gravity 1.004, molecular weight 334.5 and boiling point 217° at 1 mm of mercury:



As has been mentioned above, the six-carbon atom structure of two naphthenic rings is arbitrary, as well as the position and distribution of the paraffinic side chain consisting of 7 carbon atoms.

The average analysis of a lubricating stock is given in Table 96.

Table 96. Approximate Average Composition of a Lubricating Stock from Ponca City Crude with Respect to Rings of Molecules Containing from 20 to 40 Carbon Atoms.

Part	% of Stock	Molecular Composition	% in Given Portion	% in Entire Stock
"Water-white" oil	35	1 naphth. ring + paraf. side chain 2 naphth. rings + paraf. side chains 3 naphth. rings + paraf. side chains	92 $\left\{ \begin{array}{l} (15) \\ (45) \\ (32) \end{array} \right.$	32.2 $\left\{ \begin{array}{l} (5.3) \\ (15.7) \\ (11.2) \end{array} \right.$
		1 naphth. ring + 1 arom. ring + paraf. side chains 2 naphth. rings + 1 arom. ring + paraf. side chains	8	2.8
"Extract"	22	2 naphth. rings + paraf. side chains 3 naphth. rings + paraf. side chains	8	1.1
		2 naphth. rings + 1 arom. ring + paraf. side chains 3 naphth. rings + 1 arom. ring + paraf. side chains	25	5.5
		2 naphth. rings + 2 arom. rings + paraf. side chains 1 naphth. ring + 3 arom. rings + paraf. side chains	67 $\left\{ \begin{array}{l} (37) \\ (30) \end{array} \right.$	14.7 $\left\{ \begin{array}{l} (8.1) \\ (6.6) \end{array} \right.$
"Wax"	35	1, 2 or 3 naphth. rings + paraf. side chains Normal paraffins + possibly some iso-paraffins	50 $\left\{ \begin{array}{l} 25 \\ 75 \end{array} \right.$ to $\left\{ \begin{array}{l} 17 \\ 18 \end{array} \right.$	9 to 26
"Asphalt"	8	Probably highly condensed aromatics together with the bulk of non-hydrocarbon material of the original fraction		

Kurtz and Lipkin^{51, 61} made an attempt to determine the number of carbon atoms in the ring of lubricating-oil hydrocarbons. Their method relates to completely hydrogenated lubricating oils containing naphthenes only. They found that the molecular volume of naphthenes (as well as of paraffins) depends upon the number of chain CH_2 groups, n_1 , of ring CH_2 groups, n_2 , and of ring junction CH groups, n_3 :

$$\text{Mol vol at } 20^\circ\text{C} = 16.28 n_1 + 13.15 n_2 + 9.7 n_3 + 31.2$$

On the basis of this equation, the curves of density versus molecular weight for different ring structures were obtained, as shown in Fig. 31. The curves for the same number of rings depend on the structure of the rings, i.e. they differ for naphthenes of the cyclopentane and cyclohexane types. The spread between the specific gravity or molecular volume of a cyclohexane and a cyclopentane of the same molecular weight increases with increasing number of rings.

The first operation is the calculation of the number of rings in a naphthenic oil of a given molecular weight by the method of specific refraction or ultimate analysis (Chapter 3). The second operation is the calcula-

tion of the densities of the cyclopentane and of the cyclohexane having the same number of rings. This procedure is performed with the aid of the curves of Fig. 31. Finally one must calculate the number of carbon atoms in each ring on the basis of the density of the naphthenic oil, d , the density of cyclohexane of the same molecular weight and number of rings, d_1 , and the density of cyclopentane of the same molecular weight and number of rings, d_2 :

$$\text{Number of carbon atoms in each ring} = 6 - \frac{d_1 - d}{d_1 - d_2}.$$

For the lubricating oil cuts of the Ponca City crude, the calculation described gives 5.3 for the average number of carbon atoms in each ring. Other figures calculated from Waterman's and Bestougeff's data at least are close to this figure. Thus, according to Kurtz and Lipkin, half or more than half of the rings in lubricating oils are of the five-carbon atom (cyclopentane) type.

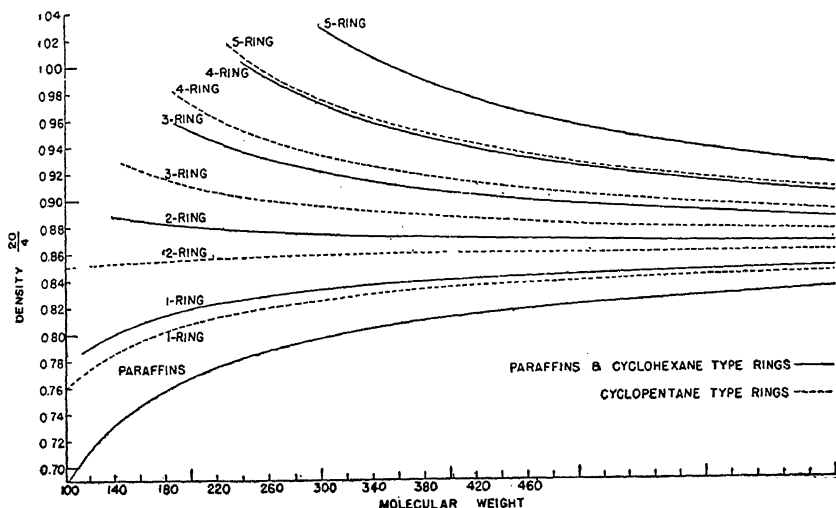


FIGURE 31. Curves of density versus molecular weight for paraffins and naphthenes of cyclopentane and cyclohexane types. (Courtesy *Industrial and Engineering Chemistry*)

It should be borne in mind, however, that any quantitative conclusions obtained on the basis of the method described seem to be premature. The number of carbon atoms per ring for hydrocarbons of the condensed mixed ring type (one cyclohexane ring and two cyclopentane rings, two cyclohexane and one cyclopentane rings) calculated by the method in question deviates from the actual number of rings (Table 4 of the original paper) by -0.4 . If this deviation is significant, the above figure of the number of carbon atoms per ring (5.3) should be corrected to 5.7. In this case the naphthenic oils should be considered as consisting to a greater extent of naphthenes having six-carbon rings.

If quantitative conclusions on the relative amount of five- and six-carbon atom rings in lubricating oils seem to be premature, the importance of the investigation of Kurtz and Lipkin remains in the proof that hydrocarbons composed of five-carbon rings must be considered as normal constituents of lubricating oils. This finding evidently is in agreement with other data pertaining to the chemical composition of petroleum. The derivatives of cyclopentane are widely distributed in gasoline fractions. In addition to this, naphthenic acids of kerosenes and gas oils have a ring structure of cyclopentane type. It is very probable that hydrocarbons of the cyclopentane type are present in gas oils and lubricating oils.

The question of the possible presence of other cyclic structures than C_5 and C_6 rings in high-boiling oil fractions will be discussed separately for naphthenic and aromatic hydrocarbons.

It should be pointed out that lubricating-oil fractions, heavily treated with sulfuric acid or solvents and consisting of naphthenes, do not show optical exaltation and have the normal value of specific refraction. Grosse (Ch. 3) summarized the data on the optical exaltation of bicyclic and tricyclic naphthenes, and confirmed that polycyclic naphthenes containing five- and six-membered rings do not show optical exaltation, whereas those having four- and particularly three-membered rings invariably do. Thus, it seems improbable that C_3 or C_4 cyclic naphthenes are present in lubricating oils in any combination with C_5 and C_6 ring structures.

The aromatic hydrocarbons of lubricating oils have high values of specific dispersion which, however, fall to the normal value of 99 after hydrogenation. This proves that the optical exaltation of lubricating-oil aromatics is due entirely to their aromatic structure. There are no C_3 or C_4 cyclic structures in the molecules of the aromatics; the latter, being unaffected by hydrogenation, would cause optical exaltation after hydrogenation.

The presence of C_7 , C_8 , etc. rings which do not display optical exaltation cannot be ruled out, but seems rather improbable in view of the absence of such hydrocarbons in gasolines. The six-membered and probably also five-membered rings should be considered as the basic ring structures of lubricating oils.

Optical rotation of heavy oil fractions, including lubricating oils, is apparently characteristic of polycyclic naphthenic structures, but the nature of the naphthenes responsible for this phenomenon is entirely unknown. Oils from naphthenic crudes are more active optically than those from paraffinic crudes. Treatment with sulfuric acid and removal of aromatic hydrocarbons does not appreciably affect the optical rotation. Carnahan *et al.*^{13a} applied optical rotation to the identification of lubricating oils. The lubricating oils of Pennsylvania crudes have a value of rotation of less than +0.26. Higher values indicate a source other than Pennsylvania.

Paraffinic Side Chains of Lubricating-Oil Hydrocarbons

The length of paraffinic side chains in hydrocarbons of lubricating oils was ordinarily calculated on the basis of molecular weight and the number of rings. For instance, the "extract" fraction, investigated by the National Bureau of Standards, had 4 aromatic and naphthenic rings and short paraffinic side chains of from 5 to 7 carbon atoms. The viscosity index of this fraction was strongly negative (Table 100). The raffinate fraction, with 3 rings and 14 carbon atoms in the side chain, had a viscosity index of 35-40. Bestougeff¹¹ calculated that the number of carbon atoms in paraffinic side chains is 16 for naphthenes from a paraffinic crude oil and 11 for those from an asphaltic crude. The viscosity index of aromatic and hydroaromatic hydrocarbons synthesized by Mikeska, with 22 carbon atoms in the side chains, exceeds 100.

These data show that the number of carbon atoms in the paraffinic side chains of medium-viscosity lubricating oils varies from 5 to 20 on the average. As has been shown above, the narrow fractions produced by solvent fractionation of a SAE 20 oil, may contain as many as 30 carbon atoms in the paraffinic side chain. The viscosity index of such fractions may be as high as 125.

Long paraffinic side chains are associated with naphthenic hydrocarbons, whereas the aromatic hydrocarbons present in lubricating oils usually have short ones. As a result, the viscosity index of the aromatic portion of lubricating oils is low, and frequently negative.

Fenske *et al.* studied the properties of very narrow fractions of lubricating stocks separated by fractional distillation and solvent treatment. They determined various properties of the fractions, including the viscosity index, which is to some extent a measure of the length of the paraffinic side chains. As stated above, the high values of the viscosity index (100 or more) correspond to paraffinic side chains longer than C_{15} . Cannon and Fenske¹² separated a dewaxed distillate from a van Zandt crude into a large number of narrow fractions by distillation and extraction with acetone. The distillate had a viscosity index of 60 and a viscosity of 780 S.U. at 100°F. The narrow fractions produced represented 0.05 per cent of the original crude oil. The viscosity index of the fractions varied from -114 to 109. The viscosity of the low viscosity-index fractions was from 920 to 11,000 and of the high viscosity-index fractions from 70 to 880 at 100°F. The authors separated a number of fractions of low viscosity index (from negative values to 10) and also of high viscosity index (90 and up); fractions of intermediate viscosity index values were practically absent. As a result, the transition from negative viscosity-index fractions to highly positive viscosity-index fractions was very sharp. Fenske and Hersh²⁵ investigated a Pennsylvania dewaxed neutral by the same method. The viscosity index of the narrow fractions varied from -320 to 140, but in this case a whole series of fractions of varied viscosity index was obtained.

The comparison with synthetic hydrocarbons of varied viscosity index

(next section) shows that the paraffinic side chains of the cyclic hydrocarbons present in lubricating oils vary from short chains of about C_5 (highly negative values of viscosity index) to very long ones of C_{20} or more (viscosity index 100 or over).

Very little is known of the structure of paraffinic side chains in lubricating oils. The occurrence of long normal paraffinic side chains (C_{12} or more) in lubricating oils of low pour point seems improbable. The derivatives of benzene, cyclohexane, naphthalene, etc. with long normal paraffinic side chains (over C_{12}) have melting points above 10°C . Such hydrocarbons, if present in original oils, would be removed with paraffin wax in the dewaxing operation. Table 97 gives the data on the melting point of various high molecular weight derivatives of cyclic hydrocarbons.

On the other hand, the corresponding derivatives of cyclic hydrocarbons with long branched paraffinic side chains may have very low pour points. The cited investigations of Mikeska, Cosby and Sutherland and others show that even a single branching, particularly in the middle of the paraffinic side chain, may be sufficient to reduce the pour point low temperatures below -10°C . Thus, it is obvious that the cyclic hydrocarbons of lubricating oils with paraffinic side chains of C_{12} or more have a branched chain structure. The degree and character of branching are entirely unknown.

Table 97. Melting Point of Alkylated Cyclic Hydrocarbons.^{16, 80}

Hydrocarbon	Melting Point ($^\circ\text{C}$)	Density (D_{40}^{20})	Viscosity in centistokes—		
			at 20°C	50°C	80°C
<i>n</i> -Dodecylcyclohexane	+12	0.8250	9.049	4.265	2.439
<i>n</i> -Tetradecylcyclohexane	+15	0.8258		5.701	3.143
<i>n</i> -Hexadecylcyclohexane	+32.5	0.8260		7.493	3.940
<i>n</i> -Octadecylcyclohexane	+40	0.834 (25°C)			
<i>n</i> -Hexadecylbenzene	+27	0.877			
<i>n</i> -Octadecylbenzene	+33	0.854 (25°C)			
<i>n</i> -Dodecosylbenzene	+42.5	0.851 (25°C)			
<i>n</i> -Octadecylnaphthalene	+51.5	0.906			
<i>n</i> -Dodecylnaphthalene	+57	0.8987			
<i>n</i> -Octadecyldecalin	+43-47	0.863			

Cracking of Lubricating Oils

The cracking of kerosenes, gas oils and lubricating oils also may give some clues to the structure of hydrocarbons present in these distillates. When the conditions of cracking are comparatively mild, the reactions are mainly those of dealkylation and dehydrogenation, and the basic ring structure may remain more or less intact. The presence of derivatives of cyclopentane, cyclohexane, benzene, naphthalene, etc. in cracked products shows that the rings of these hydrocarbons were present in the virgin stocks, either as such or in some combination with other ring structures. It seems highly probable that the hydrocarbons formed under moderate cracking conditions have approximately the same ring structure as the original ones. The formation of benzene or naphthalene, *e.g.*, can hardly be explained in any other way, since the synthesis of such hydrocarbons

from paraffins or olefins takes place at extremely high temperatures.

The cracking of paraffin wax, composed of paraffins only, produces both paraffins and olefins and almost no cyclic hydrocarbons, under moderate temperature-time cracking conditions. Ardern *et al.*¹ found that the formation of ring hydrocarbons from chain material does not occur to any appreciable extent in catalytic cracking. On the other hand, the naphthenic rings may be ruptured to some extent even under comparatively moderate cracking conditions, particularly in catalytic cracking. Thus the method in question cannot be used for quantitative determination of rings in the original stocks.

The thermal cracking of aromatic solvent extracts from lubricating distillates under rather moderate cracking conditions, at 875°F for 40 minutes, produces about 80 per cent of aromatic synthetic crude and 20 per cent of gas and coke. The liquid cracking products are highly aromatic. The fractions boiling between 70 and 200°C contain about 80 per cent of benzene derivatives, and the high-boiling fractions contain up to 90-95 per cent of aromatic hydrocarbons. Naphthalene, methyl-naphthalenes and dimethylnaphthalenes can be easily detected and separated from the fractions boiling between 215 and 270°C. The fractions boiling from 350 to 400°C contain a considerable proportion of crystalline hydrocarbons, which are apparently derivatives of anthracene and phenanthrene. Non-condensed polycyclic aromatics, such as diphenyl, were not detected, although their presence cannot be positively denied. The fractions boiling between 260 and 350°C may contain the derivatives of diphenyl and similar hydrocarbons, since the specific gravity and refractive index are much higher than those of highly alkylated naphthalenes which boil in this range. On the other hand, derivatives of tricyclic condensed aromatics should be entirely absent in these fractions.

Cracking of lubricating oils under moderate conditions gives a more complicated picture, producing a series of paraffins, naphthenes and aromatics, as might be expected in view of the more complex composition of lubricating oils compared with that of solvent tars.

Individual Hydrocarbons of Lubricating Oils

As has been pointed out, no individual hydrocarbons have so far been separated from lubricating fractions. Even the very narrow substantially constant-boiling "final homogeneous" fractions isolated by the Bureau of Standards consisted of a series of hydrocarbons, however, of similar size and type. Each of these fractions represented only 0.0025 per cent of the original Ponca City crude oil. It should be remembered that the hydrocarbons separated from lighter-boiling fractions (gasoline and kerosene) represented from 1.5 to 0.02 per cent of the original crude. This comparison shows that any individual hydrocarbon is present in lubricating oils in a much smaller percentage than in gasoline and kerosene fractions, obviously because of the tremendous number of possible isomers. The narrow fractions, representing 0.0025 per cent of the crude,

would consist of a single pure hydrocarbon for low-boiling fractions and of numerous hydrocarbons for lubricating oils.

In addition to this, the properties (boiling point, melting point, solubility, etc.) of high molecular weight hydrocarbons of approximately the same size may be very similar. As a result, the problem of separating individual hydrocarbons from lubricating oils is extremely difficult and is far from the solution.

The difference in the complexity of the composition of gasolines and lubricating oils may be illustrated by the following comparison. As stated earlier, over 75 per cent of the light Ponca City gasoline (55°-145°C) has been assigned to approximately 40 hydrocarbons. The total number of hydrocarbons composing the light gasoline will be appreciably greater than this, since the remaining 25 per cent of the gasoline consists of hydrocarbons, each of which is represented by a comparatively small percentage. Assuming the average per cent of the unseparated hydrocarbons to be 0.02 of the crude or 0.15 of the gasoline (the minimum per cent in the hydrocarbons separated), the number of unseparated hydrocarbons will be 165 and the total number of hydrocarbons in the gasoline close to 200. In any case, the total number of hydrocarbons constituting the gasoline cannot be excessive, except perhaps those present in very minute amounts.

The "final homogeneous" fractions of the lubricating stock produced by the Bureau of Standards constitute $\frac{1}{40,000}$ th part of the crude or $\frac{1}{4,000}$ th of the lubricating stock. The number of individual hydrocarbons in each fraction is unknown and can be assumed equal to the average value n , which should be much greater than 1. Thus, the total number of hydrocarbons in the lubricating stock would be $4,000n$, and would show the complexity of lubricating oils as compared to gasolines.

Synthesis of Hydrocarbons with Lubricating Properties

The synthesis of hydrocarbons, the properties of which duplicate those of lubricating oils, is another approach to the problem of the chemical composition of lubricating oils. It should be borne in mind, however, that the method of synthesis may produce hydrocarbons which have lubricating properties, but which are in all other instances quite different from lubricating oils manufactured from petroleum. For instance, polymerization of olefins under specific conditions (Chapter 5) forms high-grade synthetic lubricating oils which differ from petroleum lubricating oils in chemical composition and specific gravity, as well as in other properties. Hugel⁴¹ synthesized individual high molecular weight branched olefins ($C_{24}H_{48}$, $C_{26}H_{52}$, $C_{32}H_{64}$ and $C_{48}H_{96}$) which have a viscosity from 30 to 300 S.U. at 100°F. Hydrogenation of high molecular weight olefinic polymers gives paraffinic hydrocarbons which have lubricating properties (Chapter 5). High molecular weight isoparaffins with lubricating properties may be synthesized by other methods (Klos, Neyman-Pilat and Pilat, Cosby and Sutherland, and others).

It may be stated as a general result of these investigations that open-chain hydrocarbons, saturated or unsaturated, will have lubricating properties under two principal conditions: (1) the molecular weight of the hydrocarbons must be sufficiently high, *e.g.*, above C_{30} , to effect the required minimum limit of viscosity, and (2) the branching of the hydrocarbon should be sufficient to prevent crystallization at moderate temperatures. Such synthetic open-chain hydrocarbons with lubricating properties will differ from petroleum lubricating oils by an excess of hydrogen, by too low values of specific gravity and refractive index, by too high values of viscosity index, etc. As stated in the previous section, the petroleum lubricating oils have the ring structure.

Krämer and Spilker⁵⁰ and Spilker⁴⁸ were the first to synthesize some hydrocarbons which were fairly close to natural (petroleum) lubricating oils with respect to chemical composition. A series of hydrocarbons was produced by condensation of toluene, xylenes and pseudocumene with styrene or allyl alcohol. Both reactions take place in the presence of concentrated sulfuric acid which is added gradually to the mixture of an excess of aromatic hydrocarbon with styrene or allyl alcohol. In the second condensation two molecules of an aromatic are combined with a molecule of allyl alcohol, liberating water. Table 98 gives the formulas and viscosities of the hydrocarbons synthesized.

The first three hydrocarbons are the methylated derivatives of methyl-diphenylmethane, and the last three are those of dimethyldiphenylmethane. In both series, the viscosity of the hydrocarbons increases with the number of methyl groups. Dimethyldicumylmethane is a comparatively viscous oil.

Another method, used by Spilker, of producing more or less viscous liquid hydrocarbons was the hydrogenation of polycyclic aromatic hydrocarbons, which took place catalytically under moderate temperature conditions. The properties of hydrogenated polycyclic hydrocarbons are given in Table 99.

It should be pointed out that the original hydrocarbons (before hydrogenation) are solid crystalline substances which do not have any lubricating properties. The viscosity of liquid hydrogenated polycyclic hydrocarbons markedly increases with increasing molecular weight or number of rings in the molecule. The hydrogenated pyrene, naphthofluorene and chrysene are liquids, viscous even at comparatively elevated temperatures. The hydrogenated polycyclic hydrocarbons, however, have much higher specific gravities and are richer in carbon (or poorer in hydrogen) than natural lubricating oils of petroleum origin. These properties are obviously due to the highly polycyclic structure and the absence of any paraffinic side chains in the molecules of these hydrocarbons. Alkylation of such hydrocarbons will produce more viscous oils of lower specific gravity and richer in hydrogen, which would be closer to petroleum lubricating oils. Thus, synthetic lubricating hydrocarbons similar to those derived from petroleum can be produced either by alkylation of

polycyclic hydroaromatic hydrocarbons or by hydrogenation of alkylated polycyclic aromatics.

Table 98. Viscosities of Hydrocarbons Produced by Condensation of Aromatics.

Original Products	Structure of Condensation Product	-Viscosity (Engler)*-		
		at 20°C	50°C	100°C
Toluene-Styrene	$\begin{array}{c} \text{H} \\ \\ \text{C}_6\text{H}_5-\text{C}-\text{C}_6\text{H}_4\cdot\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	0.9	0.4	
Xylene-Styrene	$\begin{array}{c} \text{H} \\ \\ \text{C}_6\text{H}_5-\text{C}-\text{C}_6\text{H}_3(\text{CH}_3)_2 \\ \\ \text{CH}_3 \end{array}$	1.9	0.6	0.4
Pseudocumene-Styrene	$\begin{array}{c} \text{H} \\ \\ \text{C}_6\text{H}_5-\text{C}-\text{C}_6\text{H}_2(\text{CH}_3)_3 \\ \\ \text{CH}_3 \end{array}$	5.6	1.2	0.4
Toluene-Allyl alcohol	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\cdot\text{C}_6\text{H}_4-\text{C}-\text{C}_6\text{H}_4\cdot\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	3.2	0.9	0.4
Xylene-Allyl alcohol	$\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_3)_2\text{C}_6\text{H}_3-\text{C}-\text{C}_6\text{H}_3(\text{CH}_3)_2 \\ \\ \text{CH}_3 \end{array}$	16.1	2.2	0.5
Pseudocumene-Allyl alcohol	$\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_3)_3\text{C}_6\text{H}_2-\text{C}-\text{C}_6\text{H}_2(\text{CH}_3)_3 \\ \\ \text{CH}_3 \end{array}$		16.2	1.2

*Engler units are converted into Saybolt units by approximate factor 35.

Table 99. Properties of Hydrogenated Polycyclic Aromatic Hydrocarbons.

Original Hydrocarbon	—Hydrogenated Hydrocarbon—		
	D ₁₅	Viscosity (Engler) at 20°C	at 50°C
Acenaphthene, C ₁₂ H ₁₀	1.030	1.2	0.5
Fluorene, C ₁₃ H ₁₀	0.987	0.9	
Phenanthrene, C ₁₄ H ₁₀	1.035	0.5	0.6
Anthracene, C ₁₄ H ₁₀	1.002	1.5	0.4
Fluoranthene, C ₁₅ H ₁₂	1.061	7	1.8
Pyrene, C ₁₆ H ₁₀	1.076	15.5	2.3
Naphthfluorene, C ₁₇ H ₁₂	1.035	28.5	3.1
Chrysene, C ₁₈ H ₁₂	1.034		4.5

Further investigations along this line somewhat broadened the conclusions of Spilker. Any cyclic hydrocarbon, aromatic or naphthenic, monocyclic or polycyclic, alkylated with one or several sufficiently long paraffinic side chains, will have lubricating properties. The specific grav-

ity, viscosity, viscosity index, and chemical composition of such hydrocarbons will be very close to those of petroleum lubricating oils. Cetylbenzene, obtained by Tilicheyev and Kurindin¹⁰⁰ and commercial Parafflow, *i.e.*, an alkylated naphthalene with long paraffinic side chains, are examples of synthetic lubricating hydrocarbons of aromatic nature. These were obtained by the Friedel and Crafts method, *i.e.*, by condensation of aromatic hydrocarbons with olefins or halogenated paraffins in the presence of aluminum chloride.

Mikeska^{80, 81} investigated thoroughly the synthetic cyclic hydrocarbons possessing lubricating properties. They were obtained by condensation of acid chlorides with aromatic hydrocarbons in the presence of aluminum chloride. The ketones produced by this reaction were reduced to hydrocarbons by the Clemensen method. In other cases the ketones were treated with Grignard halogen compounds; the resulting alcohols were converted to olefins which subsequently were hydrogenated. By this method branched chains were obtained. A series of hydrocarbons was synthesized by the methods described, including derivatives of benzene, naphthalene, diphenyl, cyclohexane, tetralin, decalin, etc. The paraffinic or olefinic side chains consisted of from 6 to 26 carbon atoms. The position of the side chains in the nuclei has not been determined.

The following important conclusions may be summarized as a result of this investigation:

(1) Effect of ring structure:

(a) For hydrocarbons of a given molecular weight, the greater the number of rings, the higher the viscosity.

(b) Hydroaromatic hydrocarbons of a given structure have a greater viscosity but about the same viscosity index as corresponding aromatic hydrocarbons.

(2) Effect of varying the relative proportion of paraffinic to aromatic or naphthenic groups within the molecule:

(a) The viscosity index of a given aromatic or naphthenic hydrocarbon increases as the ratio of paraffinic to naphthenic or aromatic hydrocarbons is increased, the number of chains being unchanged.

(b) The effect of a given side chain on the viscosity index of hydrocarbons depends on the nature of the nucleus.

(3) Effect of the length of side chains:

(a) A long paraffinic side chain is more effective in increasing the viscosity index of a hydrocarbon than a corresponding number of carbon atoms divided between two or more side chains.

(b) On the contrary, the greater the number of side chains, the greater the viscosity, provided the number of paraffinic carbon atoms attached to a given nucleus remains unchanged.

(4) Effect of straight chains or branched chains:

(a) Straight chains are more effective in increasing the viscosity index than branched chains, provided the number of paraffinic carbon atoms remains unchanged.

(b) The effect on viscosity of the branching of the chains is indeterminate.

(5) Effect of allocation of the side chains in the nucleus:

(a) Viscosity, density and refractive index are all affected by the allocation of the side chain in the nucleus, whereas viscosity index is almost unaffected.

(6) Effect of olefinic bonds in the side chain:

(a) An olefinic bond in the side chain decreases the viscosity but scarcely affects the viscosity index.

(7) Effect of allocation of cyclic nucleus within the molecule:

(a) The allocation of cyclic nucleus within the molecule has little effect on the viscosity and viscosity index. As a result, *e.g.*, 1,1-diphenyloctodecane has about the same viscosity and viscosity index as 5,14-diphenyloctodecane.

(8) Effect of structure on pour points:

(a) Long straight chains make for higher pour points than corresponding branched chains.

(b) The increase in the number of side chains decreases the pour point, provided the number of paraffinic carbon atoms remains unchanged.

The viscosity of hydrocarbons synthesized by Mikeska varied from 42.6 to 388 Saybolt units at 100°F and from 33.2 to 58.5 at 210°F, but the viscosity index was on the average extremely high, from 100 to 196. On the average, the synthetic hydrocarbons of Mikeska with paraffinic side chains of C_{18} or more are close to Pennsylvania neutrals in viscosity and much superior in viscosity index. On the other hand, monohexylnaphthalene has a low viscosity index (−66) and dihexylnaphthalene a moderate value (53). Thus, on the assumption of the six-carbon-atom ring structure it may be postulated that the average cyclic hydrocarbons composing Pennsylvania neutrals would contain either one normal paraffinic side chain between C_{12} and C_{18} , *i.e.*, about C_{15} , or one branched side chain of about C_{18} or somewhat longer, or a number of shorter side chains having a total number of carbon atoms of 18 or more. It should be remembered that the branching of a paraffinic side chain as well as the splitting of a long paraffinic side chain into a number of shorter side chains has a depressing effect on the viscosity index.

These conclusions at least do not contradict those obtained on the basis of the analytical data. For instance, the determinations of Rossini show that a narrow fraction of a Mid-Continent viscous neutral oil (viscosity 350–380, V.I. 35–40) contains 14 carbon atoms in paraffinic side chains. Viscous aromatic extract fractions with strongly negative values of viscosity index have a much lower number of paraffinic carbon atoms—from 5 to 7 (Table 100). Bestougeff¹ also calculated the number of carbon atoms in the paraffinic side chains of paraffin-base lubricants to be 16 and that of asphaltic lubricants 11.

Referring to the above general conclusions of Mikeska, it should be

pointed out that 1b on the effect of hydrogenation of aromatics is in apparent contradiction to the data pertaining to hydrogenation of oil fractions. It is well known that the hydrogenation of straight-run oil fractions, resulting in the transformation of aromatics into hydroaromatics, invariably decreases the viscosity. Table 100 includes the data of Mikeska and Neyman-Pilat and Pilat on the effect of hydrogenation of some synthetic aromatic hydrocarbons, and those of Rossini⁹⁰ on the effect of hydrogenation of some "homogeneous" lubricating fractions produced from a Mid-Continent crude oil. The difference between the results of hydrogenation of synthetic aromatics and oil fractions is striking. The positive effect of hydrogenation upon the viscosity of monocyclic and bicyclic aromatics, however, is not very significant: the increase in viscosity at 100°F due to hydrogenation does not exceed 40 per cent. The negative effect of hydrogenation upon the viscosity of a tricyclic "homogeneous" fraction with one aromatic ring is insignificant, and does not exceed 10 per cent. On the contrary, the negative effect of hydrogenation upon the viscosity of tetracyclic "homogeneous" fractions with 2 or 3 aromatic rings is substantial. As a result of hydrogenation, the viscosity at 100°F decreases many times. Thus it seems probable that the negative effect of hydrogenation upon the viscosity of oil fractions is due to the highly polycyclic structure of aromatic hydrocarbons present in lubricating oils. Apparently, the viscosity of tricyclic or tetracyclic naphthenoaromatic hydrocarbons decreases on hydrogenation.

Cosby and Sutherland¹⁸ recently synthesized a few derivatives of benzene, cyclohexane and decalin with long paraffinic side chains, which possess lubricating properties. Their conclusions are similar to those of Mikeska. They also found that the viscosity of monocyclic and bicyclic aromatic hydrocarbons increases on hydrogenation.

A series of cyclic hydrocarbons with 22 carbon atoms per molecule was synthesized by Neyman-Pilat and Pilat. The position of the side chains was determined. The hydrocarbons were derivatives of benzene, cyclohexane, dicarvacrylethane and diperhydrocarvacrylethane. All these hydrocarbons have lubricating properties.

Synthetic high molecular weight aromatics were used by Robinson⁸⁷ for determining the nature of aromatic hydrocarbons in lubricating oils. The method was as follows. To a dearomatized lubricating oil fraction, synthetic aromatic hydrocarbons of different types were added, in an amount corresponding exactly to the actual amount of "natural" aromatics in the original fraction. The physical properties (specific gravity and refractive index) of these mixtures were compared with those of the initial fraction. Monocyclic aromatics with long paraffinic side chains gave maximum deviations from the initial fractions. Dicyclic aromatics with shorter paraffinic side chains, tricyclic aromatics with paraffinic side chains in higher-boiling fractions, and monocyclic aromatics with naphthenic rings in the side chains, gave mixtures close to natural fractions. It has been concluded that the "natural" aromatics removed by

dearomatization should be close to the polycyclic aromatic hydrocarbons with comparatively short side chains, or to the monocyclic aromatics with naphthenic rings in the side chains.

Koch and Steinbrink⁴⁸ synthesized hexaethyl- and tetraisopropylcyclohexane, which have the properties of high-grade spindle oils. Hence, even short paraffinic side chains in a sufficient number may produce lubricating properties. Schmidt and Grosser⁹⁷ studied the derivatives of benzene and diphenyl with long paraffinic and olefinic side chains.

Schiessler *et al.*⁹⁵ recently reported on the properties of 42 synthetic hydrocarbons, C_{25} to C_{32} , with lubricating properties, including paraffins, naphthenes and aromatics with long paraffinic side chains. The principal reaction used to produce the hydrocarbons was the Grignard preparation of alcohols followed by dehydration and hydrogenation of the olefins formed.

Table 100. Viscosity and Viscosity Index of Aromatic Hydrocarbons, "Homogeneous" Lubricating Fractions, and Hydrogenated Products Thereof.

Molecular Formula	Number of Rings		Character of Rings	No. of C-atoms in Paraffin Side Chain	—Kinematic Visc—		V.I.
	Naphth	Aromat			at 100°F	210°F	
$C_{25}H_{50}$	0	1	1 ring	22	0.1657	0.0372	138*
$C_{28}H_{56}$	1	0	" "	22	0.1960	0.0417	140
$C_{28}H_{44}$	0	2	2 condensed rings	18	0.2286	0.0463	140*
$C_{28}H_{54}$	2	0	" "	18	0.3080	0.0586	144
$C_{34}H_{54}$	0	2	2 non-condensed rings	22	0.5680	0.0760	111*
$C_{34}H_{66}$	2	0	"	22	0.7620	0.0910	110
$C_{22}H_{38}$	0	1	1 ring	16		0.024	†
$C_{22}H_{44}$	1	0	" "	16		0.026	†
$C_{22}H_{30}$	0	2	2 rings	10		0.032	†
$C_{22}H_{42}$	2	0	" "	10		0.039	†
$C_{23}H_{26}$	1	3	condensed rings	5	90	0.26	—1600†
$C_{23}H_{40}$	4	0	" "	5	3.5	0.10	—300
$C_{25}H_{34}$	2	2	" "	7	16	0.20	—365†
$C_{25}H_{44}$	4	0	" "	7	3.5	0.12	—150
$C_{28}H_{46}$	2	1	" "	14	0.83	0.078	35†
$C_{28}H_{52}$	3	0	" "	14	0.76	0.075	40

* Mikeska⁹⁰.

† Neyman-Pilat *et al.*⁹¹.

‡ Rossini⁹².

While the general conclusions of Mikeska have been in general confirmed, the following results are of importance. Though branching, particularly multiple branching ("clustering"), has relatively little effect on refractive index and density, it has a marked influence on viscosity, viscosity index, and boiling point: the viscosity increases and the viscosity index decreases because of clustering of the molecules. Isoparaffins ($C_{26}H_{54}$) with two branches (C_4 or C_6) in the central parts of the molecule have comparatively moderate values of viscosity index (72 and 84),

whereas less branched paraffins of the same or almost the same molecular weight have a viscosity index much above 100.

The migration of a phenyl or cyclohexyl group along a 20-carbon straight chain has a complex effect on the viscosity: as the ring is moved from the center toward the end of the paraffin chain, the viscosity passes through a maximum corresponding to position 5, while the viscosity index rapidly and continuously increases. The same phenomenon was studied by Schmidt and Grosser.⁹⁷

The last paper by Schiessler *et al.*⁹⁸ covers a new series of synthetic hydrocarbons with lubricating properties (from C₂₅ to C₂₈). Hydrocarbons containing from one to three cyclopentyl rings were synthesized. The effect of unsaturation was also studied. The hydrocarbons with cyclopentyl rings are of particular interest. Their viscosity and viscosity index may differ considerably from those of hydrocarbons having the cyclohexyl structure with the same number of carbon atoms. Various polycyclopentyls were synthesized by von Braun and Reitz-Kopp^{3a} and by Goheen.^{33a}

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Chapter 5

Hydrocarbons of Synthetic Distillates

This chapter is confined to synthetic fuels, synthetic lubricating oils and similar products, which have the properties of natural petroleum products and are manufactured from petroleum by thermal and catalytic processes. In contrast to straight-run distillates and fractions, synthetic distillates are the result of the chemical transformation of oil products effected by high temperature (cracking), action of hydrogen (hydrogenation), action of catalysts, etc. In some cases the synthetic distillates are predominantly paraffinic or olefinic, but in most cases they include four classes of hydrocarbons, *i.e.*, paraffins, unsaturates, naphthenes and aromatics. The unsaturates may be open-chain olefins, cyclic olefins and diolefins, as well as various combinations of cyclic hydrocarbons with unsaturated side chains.

Various chemicals produced from petroleum are beyond the scope of this volume.

Synthetic Paraffins

Synthetic low and medium molecular weight paraffins are produced commercially by two methods: hydrogenation of polymerized olefins and alkylation of paraffins, mostly isoparaffins, with olefins.

The polymerization of olefins, catalytic or non-catalytic (thermal), may yield various hydrocarbons including polymerized olefins, paraffins, naphthenes, and aromatics. As will be seen later, the formation of the last three is due to secondary reactions. Evidently, the hydrogenation of such polymerized products will also form a mixture of hydrocarbons of various classes. It should be pointed out, however, that the hydrogenation of such polymers is not used commercially.

When the polymerization of olefins takes place under certain conditions, particularly by catalysis at low temperatures, it can be directed selectively to polymerization without any side reactions, forming other classes of hydrocarbons. For instance, butenes and isobutene can be polymerized into dimers (and trimers) by the catalytic action of sulfuric acid at temperatures not exceeding 100°C, or of phosphoric acid at temperatures not over 200°C. Hydrogenation of such true polymers, also under moderate temperature conditions, yields pure synthetic paraffins. Commercial isooctane is obtained by this method.

Catalytic low-temperature alkylation of isobutane with butenes and isobutene in the presence of sulfuric or hydrofluoric acid gives a paraffinic

alkylate consisting almost quantitatively of paraffins. Thermal alkylation of isobutane with olefins, particularly with ethene, produces a mixture of alkylated paraffins with some polymerized olefins. The paraffins may be separated from the olefins by careful fractionation or by suitable treatment.

Commercial isooctane produced from isobutene consists predominantly of 2,2,4-trimethylpentane. Brooks, Cleaton and Carter^s fractionated pure commercial isooctane which gave 1.25 per cent of forerun and 2.16 per cent of still residue, before and after the separation of pure (99 per cent) 2,2,4-trimethylpentane. The forerun and still residue were fractionated by distillation and crystallization; and the hydrocarbons listed in Table 101 were identified and determined.

Table 101. Hydrocarbons Accompanying 2,2,4-Trimethylpentane in Commercial Isooctane.

Hydrocarbon	Identification	Percentage
Boiling Below 2,2,4-Trimethylpentane		
2,2-Dimethylbutane	Probable	0.01
2,3-Dimethylbutane	Possible	0.03
2-Methylpentane	do	0.02
2,2-Dimethylpentane	do	0.19
2,4-Dimethylpentane	do	0.03
2,3-Dimethylpentane	Probable	0.01
2-Methylhexane	do	0.02
Boiling Above 2,2,4-Trimethylpentane		
2,4-Dimethylhexane	do}	0.04
2,5-Dimethylhexane	do}	
3,3-Dimethylhexane	do	0.04
2,3,4-Trimethylpentane	Positive	0.12
2,3,3-Trimethylpentane	do	0.10
2,2,5-Trimethylhexane	do	0.50
2,2,4-Trimethylhexane	Probable	0.10
2,4-Dimethylheptane	Doubtful	0.03
3,3-Dimethylheptane	do	0.04
4-Ethylheptane	do	0.01
2,2,6-Trimethylheptane	Positive	0.13
2,2,4- or 2,2,5-Trimethylheptane	Probable	0.02
2,6-Dimethyloctane	Very doubtful	0.02
3,3,4,4-Tetramethylhexane	Probable	0.04
2,2,3,3,4-Pentamethylhexane	Very doubtful	0.02

It should be pointed out, however, that pure commercial isooctane is obtained by fractionation of hydrogenated diisobutene. The original hydrogenated dimer contains a larger proportion of other isomers.

Commercial hydro-codimer produced from copolymers of butanes, *i.e.*, by copolymerization of normal butenes and isobutene and further hydrogenation, is much richer in other isomers, particularly 2,2,3-, 2,3,3- and 2,3,4-trimethylpentane. The percentage of each of the above isomers is usually of the same order as that of 2,2,4-trimethylpentane.

The alkylates formed by alkylation of isobutane with olefins consist of many paraffins of various structures and molecular weights. First of all, the structure of the alkylated paraffins usually does not correspond to the direct alkylation or simple addition of the isoparaffin to the double

bond. Instead of a single or few hydrocarbons of the expected structure, various isomers may be formed. In addition to this, paraffins of a lower and higher molecular weight are formed, evidently as a result of secondary cracking reactions and further realkylation of the olefins formed. The theories advanced to explain the mechanism of the alkylation are beyond the scope of this volume.

The average composition of a commercial alkylate may be represented as follows:

Isopentane	up to 10 per cent
2,2,4-Trimethylpentane	from 25 to 45 per cent
2,2,3-Trimethylpentane	less than 5 per cent
2,3,3-Trimethylpentane	from 15 to 25 per cent
2,3,4-Trimethylpentane	" 15 " 30 " "
Dimethylhexanes	up to 20 per cent
Isohexanes and isoheptanes	up to 20 per cent

If the alkylate is produced from C_3 and C_4 olefins, the proportion of isoheptanes will be much higher, depending upon the concentration of propene in the gas. The composition of the charging stock (olefins, isobutane or isopentane) affects the composition of the alkylate to a much greater extent than the nature of the catalyst (sulfuric acid, hydrofluoric acid, or aluminum chloride).

Birch and Dunstan⁸ and McAllister, Anderson, Ballard and Ross²⁹ investigated thoroughly the alkylates produced by interaction of isobutane with various olefins in the presence of sulfuric acid. The results of the two investigations are fairly close and are summarized in Table 102.

Pines, Grosse and Ipatieff³⁴ alkylated isobutane with normal butenes or propene at low temperatures (30° - 35°C) in the presence of aluminum chloride and studied the chemical composition of the alkylates produced. In general, the composition was identical with the data of Table 94. The isobutane-*n*-butenes alkylate contained 60 per cent octanes: mostly 2,2,3-, 2,2,4- and 2,3,4-trimethylpentane and 2,5-dimethylhexane. The isobutane-propene alkylate contained 40 per cent heptanes: mostly 2,3- and 2,4-dimethylpentanes.

It is of interest to note that the alkylates produced by low-temperature catalytic alkylation have approximately the same composition regardless of the catalyst used. Thus, sulfuric acid, aluminum chloride, hydrogen fluoride, boron fluoride, used as catalysts, form very similar alkylates from isobutane and a certain olefin.

Thermal alkylation under suitable temperature-pressure conditions produces alkylates of a composition different from those obtained with the low-temperature catalytic processes. Oberfell and Frey³¹ give the following composition of the products obtained by the alkylation of isobutane with ethene at 515°C (959°F) and 4500 lbs/sq in pressure (Table 103).

Thus, in contradistinction to the alkylates produced catalytically at low temperatures, thermal alkylates contain an appreciable proportion of polymerized olefins (about 15 per cent in all), which are formed by

Table 102. Hydrocarbons Identified in Alkylates Produced from Isobutane.

Olefin Used	Hydrocarbons Produced	% by Weight
Propene	2,4-Dimethylpentane	8-12
	2,3-Dimethylpentane	62-66
	2,2,4-Trimethylpentane	5-9
	2,3,4- or 2,3,3-Trimethylpentane	6-10
	Propane	
Butene-2	2,3-Dimethylbutane	
	Isopentane	trace
	2,3-Dimethylbutane	4-6
	2,2,4-Trimethylpentane	34-38
	2,3,4- or 2,3,3-Trimethylpentane	51-55
Butene-1, butene-1,2-diisobutene	Isobutane (probably)	
	2,2,4-Trimethylpentane	
	2,5-Dimethylhexane	
	2,4-Dimethylhexane	
	2,2,5-Trimethylhexane	
	2,3-Dimethylbutane	
	2-Methylpentane	
	2,2,6-Trimethylheptane (?)	
	Isopentane	
	Isopentane	7-9
Isobutene	2,3-Dimethylbutane	8-10
	2,2,4-Trimethylpentane	24-28
	2,3,4- or 2,3,3-Trimethylpentane	30-34
	Isobutane probably	
	Isopentane	6-8
Pentene-2	2,2,4-Trimethylpentane	6-10
	2,3,4- or 2,3,3-Trimethylpentane	8-12
	Isononanes	56-65
2-Methylbutene-2	Isopentane	18-20
	2,3-Dimethylbutane	5-7
	2,2,4-Trimethylpentane	14-16
	2,3,4- or 2,3,3-Trimethylpentane	15-17
	Isononanes	15-20
	Methylcyclopentane	5-6
Cyclohexene	Cyclohexane	4-5
	2,2,4-Trimethylpentane	4-6
	2,3,4- or 2,3,3-Trimethylpentane	4-5
	C ₁₀ -subst. cyclopentanes (?)	15-20
	C ₁₀ -subst. cyclohexanes (?)	50-55

side polymerization reactions. A predominant paraffin is 2,2-dimethylbutane, or neohexane, formed by simple addition of isobutane to the double bond of ethene. It is interesting that the catalytic alkylation of isobutane with ethene at low or moderate temperatures in the presence of aluminum chloride yields 2,3-dimethylbutane and no neohexane.

Commercial synthetic paraffinic fuels, *i.e.*, commercial "isooctane" and alkylates, have properties corresponding to their highly branched paraffinic structure. The octane number of such fuels is very high—about 98 for commercial isooctane, 93-95 for alkylates produced from butenes and isobutane, and 83-84 for neohexane alkylate (Motor Method). The response to tetraethyl lead and the stability are excellent. Accordingly, the synthetic paraffins are widely used with isopentane as high-octane constituents of aviation fuels, in combination with some selected natural, straight-run, or catalytically cracked gasolines. Leading of these blends with 3 or 4 cc of tetraethyl lead (per gallon) gives fuels

of 100 octane. The proportion of isooctane or alkylate in such blends is usually from 40 to 60 per cent. Some aromatic hydrocarbons may be used in them, particularly in fighting-grade aviation fuels; and they are beneficial for operation under supercharging conditions.

Table 103. Hydrocarbons of Thermal Alkylate Produced from Isobutane and Ethene.

Hydrocarbon	Percentage
Pentenes	1.9
Pentanes	5.0
Hexenes	5.2
2,2-Dimethylbutane (Neohexane)	42.1
2,3-Dimethylbutane	17.5
2-Methylpentane	
<i>n</i> -Hexane	
C_7H_{14}	2.4
C_7H_{16}	4.1
C_8H_{16}	3.2
C_8H_{18}	12.7
C_9 to 200°C (392°F)	4.8
Heavier	1.1
Total	100.0

Synthetic high molecular weight normal paraffins are made by the Fischer-Tropsch process, of which the above paraffins are a by-product. Under specific conditions (high pressures and with ruthenium as a catalyst), high molecular weight paraffins are obtained as a main product (Pichler and Buffleb²³). The molecular weight of such paraffins may be above 8,000 and the melting point above 130°C. It is of interest that the melting point of high molecular weight paraffins approaches asymptotically 145°C. Liquid paraffins of such high molecular weight have the properties of resins.

Polymer Gasolines

The composition of polymer gasolines depends mostly upon the conditions under which the olefins are polymerized. If the conditions are mild, the polymers formed consist almost entirely of monoolefins.

Lebedev and Kobliansky²⁵ found that the polymers formed from isobutene at room temperature over Floridin are purely olefinic and consist predominantly of di-, tri- and tetramers. As stated above, polymerization of isobutene and butenes in the presence of sulfuric acid below 100°C yields mostly dimers and trimers (about 15 per cent). Ipatieff and Corson²¹ found that the polymers of isobutene obtained at 30°C over phosphoric-acid catalyst consisted almost entirely of two individual hydrocarbons, one corresponding to diisobutene and the other to triisobutene. According to Ipatieff, polymers from polymerization of propene at 135-200°C under 1 to 15 atmospheres' pressure also consist of monoolefins. If the temperature and pressure conditions are more severe, naphthenes and aromatics are formed as a result of secondary reactions. Ipatieff and Pines²² give the following composition of a polymer gasoline produced by catalytic polymerization (over phosphoric-acid catalyst) at 330°C in a batch operation:

Paraffins	15 per cent
Olefins, incl. cyclic	69 " "
Naphthenes	10 " "
Aromatics	6 " "

It should be pointed out that the determination of unsaturates in polymer gasolines by iodine or bromine numbers frequently gives results which are too high (sometimes more than 100 per cent) due to the substitution reaction with highly branched olefins (page 171). Thus determination of the percentage of unsaturates in such gasolines is not reliable unless special precautions or modifications of the method are employed.

Little is known of the structure of the olefins formed as a result of polymerization. Whitmore and his co-workers^{49, 50} investigated the diisobutenes formed by polymerization of isobutene. The polymer consists mostly of 2,2,4-trimethylpentene-1 and partially of 2,2,4-trimethylpentene-2.

Hoog, Smittenberg and Visser²⁰ polymerized propene, normal butenes and isobutene over solid phosphoric-acid catalyst under mild conditions (160-260°C, 40 atm). The polymers were hydrogenated into corresponding paraffins, and then fractionated. The polymerization and subsequent hydrogenation of propene gave mostly nonanes and decanes. The primary polymerization product, hexene, reacts further with propene and forms nonenes and decenes. In the presence of less active catalysts, *e.g.*, alumina on silica, however, polymers containing over 50 per cent hexenes were obtained. The main component of the hydrogenation product was found to be 2-methylpentane.

Normal butenes on polymerization gave mostly octenes (50 per cent) and dodecenes (20 per cent). The hydrogenated product contained a considerable quantity of 2,3- and 2,4-dimethylhexane. The polymerized and hydrogenated isobutene consists of 2,2,4- and 2,3,4-trimethylpentane (70 per cent and 15-20 per cent, respectively). Cross-polymerization of isobutene and propene and subsequent hydrogenation gave 2,2- and 2,3-dimethylpentane and 2,2,4- and 2,3,4-trimethylpentane.

The chemical composition of polymerized products is much more complicated than would be expected on the basis of simple polymerization. The mechanism of polymerization is not at all clear. In addition, the primary polymers or dimers formed may be rearranged and/or further polymerized. The rearrangement or isomerization of 2,2-dimethylbutane into 2,3-dimethylbutane over a phosphoric-acid catalyst was confirmed experimentally by the above authors.

Pure olefinic polymer gasolines are produced commercially only for further hydrogenation and the manufacture of isooctane. As stated above, such purely olefinic polymers are formed under mild conditions of catalytic polymerization in the presence of sulfuric or phosphoric acid. Otherwise, commercial polymer gasolines, produced under more severe conditions, usually have a more complex composition similar to that indicated in the beginning of this section.

Tongberg and his associates⁴⁵ studied the composition of a commercial polymer gasoline by fractionation in a column corresponding to 100 theoretical plates. The gasoline was produced by catalytic polymerization of cracked gases containing 25 per cent of propene and butenes at 232°C (450°F) over solid phosphoric-acid catalyst (U.O.P. process). The properties of the gasoline were: 66.2° A.P.I.; A.S.T.M. distillation from 58°C (136°F) to 220°C (428°F), octane number 81 (MM). The following conclusions were drawn by the authors:

(1) Polymer gasoline contains a large proportion of heptenes and octenes which distill in the fraction between 80 and 110°C, the size of this fraction being about 49 per cent;

(2) Bromine numbers of the fractions obtained were too high for monoolefins, probably because of substitution (compare page 171);

(3) Aromatics, cyclic olefins and diolefins are present in comparatively small amount, since the refractive index curve of the fractions obtained does not show pronounced peaks and valleys.

The conditions of thermal polymerization of hydrocarbon gases are much more severe than those of the catalytic processes. The temperature in the thermal process is from 550°C (1022°F) to 600°C (1112°F) or higher, and the pressure up to 3,000 lbs/sq in. It is understandable that under these conditions the polymerization reactions proper play only a comparatively unimportant part, and that other reactions, including decomposition, condensation, etc., take precedence. As a result, the composition of thermal polymer gasolines differs substantially from that of catalytically polymerized gasolines. As a matter of fact, the former strongly resemble conventional cracked gasolines. The composition of a thermal polymer naphtha was investigated by Tannich *et al.*⁴¹ (Table 104). The naphtha was produced at 1020-1030°F at 1,700 lbs pressure.

Table 104. Hydrocarbons in Butane-free Light Thermal Polymer Naphtha: A.P.I. 71.3°, A.S.T.M. distillation from 108° to 207°F (95%).

Fraction	Saturates (%) [*]	Unsaturates (%) [*]
Isopentane	7.8	4.0
<i>n</i> -Pentane	8.2	7.2
Cyclopentane	4.6	3.1
Isomeric hexanes	10.1	6.8
<i>n</i> -Hexane	4.7	2.5
Isomeric heptanes	19.8	8.9
<i>n</i> -Heptane	4.3	1.8
Heavier	3.7†	2.5†
Total	63.2	36.8

^{*}With reference to the total naphtha.

†Calculated from the total percentage of this fraction 6.2, assuming the relative proportion of unsaturates to be 40 per cent.

It is understood that the fractions of Table 104 contain not only the hydrocarbons indicated but also others boiling in the same range. However, the percentage of isopentane, *n*-pentane, and pentenes should be close to the figures given, since other hydrocarbons, naphthenes and

aromatics are practically absent in the boiling range of these fractions. Thus, the following content of C_5 hydrocarbons may be accepted:

Isopentane	7.8	per	cent	by	vol	of	total	naphtha
<i>n</i> -Pentane	8.2	"	"	"	"	"	"	"
Pentenenes	11.2	"	"	"	"	"	"	"

The "thermally polymerized" gasoline studied by Tannich *et al.* has been produced under comparatively moderate temperature conditions. The content of aromatics in such gasolines is moderate. If "thermal polymerization" takes place at much higher temperatures, *e.g.*, 650°C (1002°F) or higher, polymerized gasolines with a high percentage of aromatics are produced (Cooke *et al.*¹⁰).

The properties of polymerized gasolines are closely related to their chemical composition. The clear octane number of such gasolines is about 80-82 (MM), but their response to tetraethyl lead is usually poor, particularly for catalytically polymerized and highly aromatic gasolines containing a large percentage of unsaturates or aromatics. Moreover, they are unstable being easily oxidized on storage.

Cracked Gasolines

Percentage of Various Classes of Hydrocarbons.—In addition to the paraffins, naphthenes and aromatics, present in straight-run gasolines, cracked gasolines contain unsaturates, including open-chain and cyclic olefins, diolefins, and cyclic hydrocarbons with olefinic side chains. The total amount of unsaturates can be determined by the methods described in Chapter 3. Many data on the composition of cracked gasolines were obtained by various unreliable methods, such as by treatment with 80-90 per cent sulfuric acid for determining unsaturates and by subsequent treatment with 96-100 per cent acid for determining aromatics. Such doubtful data are not included in the tables of this chapter. It should be remembered that even more reliable methods of determining unsaturates, discussed in Chapter 3, give only approximate figures. The chemical composition of various cracked gasolines is given in Table 105, according to the data of Faragher *et al.*,¹³ Garner,¹⁵ Bates *et al.*,² Anon.,¹ and of the author.

The chemical composition of cracked gasolines made by the mixed-phase process depends upon the nature of the charging stock. The naphthenic and asphaltic crudes (Smackover, Panuco) yield cracked gasolines having a higher content of naphthenes and aromatics. The content of naphthenes, however, is small even in gasolines from naphthenic stocks, as compared with straight-run gasolines. The content of unsaturates varies in a comparatively narrow range from 30 to 40 per cent.

The composition of reformed gasolines is close to that of mixed-phase cracked gasolines, but the content of aromatics is appreciably higher.

Polyformed and hydroformed gasolines contain a large percentage of

aromatics. The polyforming or gas reversion process is carried out in the presence of hydrocarbon gases, such as butane or propane.⁶ The temperature conditions of these processes are more severe than in conventional cracking, resulting in an increased proportion of aromatics. The hydroforming process is accompanied by dehydrogenation of cyclohexanes and by partial cyclization of the paraffins into aromatics in the presence of catalysts, which also results in a high percentage of aromatics.³⁷ The aromatic content in such gasolines may be as high as 50 per cent. At the present time commercial production of toluene by these processes is taking place on a large commercial scale.

Table 105. Chemical Composition of Cracked Gasolines.
(End Point 400°F)

Charging Stock	Per cent by weight			
	Aromatics	Unsaturation	Naphthenes	Paraffin
<i>Mixed-phase Non-catalytic Process</i>				
W. Texas topped crude	13.1	30.8		
Panhandle gas oil	10.5	32.8		
Seminole fuel oil	9.0	29.1		
Smackover crude	16.0	29.1		
Panuco crude	15.6	27.3		
Pennsylvania crude	7.1	34.6		
Grozny waxy gas oil	7	31	16	45
Surachany waxy fuel oil	4	39	13	44
Oklahoma City gas oil	10	39	16	35
Light gas oil, mixed-base	8.5	30	15	46.5
Heavy gas oil, same	6.5	41	9	43.5
Residuum, same	6	45	8	41
Kerosene naphthenic	9	24	35	32
Residuum naphthenic	6.5	36.5	11.5	46
<i>Vapor-phase Cracking</i>				
Mixed gas oil (DeFlorez)	16	49	25	10
Gas oil (Gyro)	23	45	14	19
<i>Catalytic (Houdry) Process</i>				
Gas oil, low space rate (1:1)	15	18	23	44
E. Texas naphtha (reforming)	17.3	10.0	23.4	49.3
Gas oil, A.P.I. 31°	16	8	21	47
Reduced coastal crude	18	24	24	34

Vapor phase-cracked gasolines have a higher percentage of olefins and aromatics. The percentage of aromatics is not necessarily great in these gasolines, unless the temperature of the process is very high, above 600°C (1112°F). The paraffin content of vapor phase-cracked gasolines is small. At very high temperatures of cracking—700°C (1292°F) to 800°C (1472°F)—highly aromatic gasolines containing 50 per cent or more of pure aromatics are obtained. These gasolines are also rich in unsaturates, including diolefins, cyclic olefins, and styrene.

High-temperature cracking of hydrocarbon gases also yields highly aromatic gasolines. Dunstan and Howes¹¹ have given the data on the properties of gasolines obtained from oil-field gases at temperatures from 700 to 850°C. These gasolines, obtained at 800 to 850°C, contained chiefly benzene and toluene, and approximately 20 per cent unsaturates.

Under less severe conditions, at 700 to 750°C, the content of olefins was much higher.

Catalytically cracked gasolines (produced in the Houdry or similar processes using clays or synthetic alumina-silica catalysts) differ substantially in their chemical composition from thermally cracked gasolines. In general, the content of unsaturates is comparatively small, which causes the great stability of such gasolines. The aromatic content is larger than in thermally cracked gasolines but is not particularly high, usually not exceeding 15-20 per cent on the average. Catalytic reforming, or so-called two-pass catalytic cracking, produces gasolines with an aromatic content amounting to 25-30 per cent. The content of paraffins is usually great, approximately 45-50 per cent. As will be seen later, the paraffins of catalytic gasolines are predominantly isoparaffins; thus these gasolines have high octane numbers.

It should be pointed out, however, that the composition of catalytic gasolines depends not only upon conventional cracking conditions, such as temperature, charging stock, etc., but also upon factors relating to the catalyst. The space rate, *i.e.*, the volume of the charging stock per volume of catalyst per hour, for a stationary catalyst (Houdry) and the relative amount of catalyst for a given soaking time in the case of a continuous process (Standard Oil Co. of New Jersey) bear strongly on the chemical composition of gasolines obtained. Another factor is the activity of the catalyst, which changes during operation, being great in the early stages and decreasing gradually and rapidly with time because of deposition of coke. As a result, in the Houdry process, for instance,

Table 106. Fractional Distribution of Hydrocarbons in Cracked Gasolines.

Fraction (°C)	Percentage by Weight			
	Aromatics	Unsaturates	Naphthenes	Paraffins
<i>Cracked Gasoline from Smackover Crude (Mixed-phase Process)</i>				
0-45		24		
45-64		33.3		
64-95	3.5	43.2		
95-125	7.9	35.7		
125-150	16.1	29.9		
150-180	21.4	29.8		
<i>Cracked Gasoline from Grozny Paraffinic Gas Oil (Mixed-phase Process)</i>				
Below 60	0	53	0	47
60-95	1	33	14	52
95-122	5	29	18	48
122-150	8	29	16	47
150-200	12	25	22	41
<i>Cracked Gasoline from Surachany Paraffin-Base Fuel (Mixed-phase Process)</i>				
Below 60	0	45	0	55
60-95	1	36	10	53
95-122	1	40	16	43
122-150	5	37	18	40
150-200	8	37	17	38

the chemical composition of gasoline in the first five minutes of the reaction will be different from that in the tenth minute. It is evident that the distinction between thermally and catalytically cracked gasolines becomes less and less significant at high space rates or/and in advanced stages of catalytic cracking, when the catalyst is appreciably deactivated. Highly unsaturated catalytic gasolines containing as much as 50 per cent unsaturates can be produced under such conditions.

The catalytically cracked gasolines from the Cycloversion process, produced at high temperatures up to 1200°F in the presence of steam, are more unsaturated than other catalytically cracked gasolines and contain from 60 to 80 per cent of unsaturates (calculated on the basis of bromine numbers from 90 to 125, and possibly somewhat exaggerated, as has been discussed in Chapter 3).

Faragher, Morrell and Levine¹³ and Sachanen and Tilicheyev³⁸ separated thermally cracked gasolines into fractions boiling in the range of the principal aromatic hydrocarbons and determined their chemical composition. The results are given in Table 106. The content of olefins as well as of paraffins decreases with increasing boiling range of the fraction. The low olefin content in the first two low-boiling fractions of Smackover cracked gasoline seems rather exceptional. The aromatic content increases with increasing number of the fraction, as is also observed for straight-run gasolines. The small content of naphthenes varies within comparatively narrow limits.

The distribution of hydrocarbons in the fractions of catalytically cracked gasolines gives approximately the same picture. The increase of the aromatic content with increasing boiling range, however, for such gasolines is much more rapid than for thermal gasolines. As a result, heavy naphthas (boiling range from 300-350°F to 425°F) of catalytic gasolines are highly aromatic. According to Holaday,¹⁹ Houdry-cracked naphtha (specific gravity 0.85 and boiling range from 330 to 397°F) has the following composition:

Olefins	4 per cent
Aromatics	36 " "
Naphthenes and paraffins	60 " "

Bates, Kurtz, Rose and Mills² also found a high content of aromatics in catalytically cracked heavy naphthas.

The content of diolefins in cracked gasolines will be discussed in the next section.

Individual Hydrocarbons in Cracked Gasolines.—The knowledge of individual hydrocarbons in cracked gasolines is very meager. Of the aromatic hydrocarbons, benzene occurs in a very insignificant proportion in commercial mixed-phase cracked or catalytic gasolines. As the data of Table 106 clearly show, toluene and high-boiling alkyl derivatives of benzene predominate. The average proportion of benzene in cracked gasolines (400°F end point) from mixed-base charging stocks (mixed-

phase process) does not exceed 0.2 per cent, of toluene 1 per cent, and of xylenes plus ethylbenzene $1\frac{1}{2}$ per cent.

As described above, the percentage of individual low molecular weight aromatics, *i.e.*, benzene and toluene, is high in vapor phase-cracked gasolines produced under high-temperature conditions (700°C or 1292°F), amounting to 15 per cent for benzene and 20 per cent for toluene. Poly-formed gasolines contain on the average 5 per cent of toluene and 8-10 per cent of C_8 -aromatics.

Tannich, Thomas and Padgett⁴¹ separated a cracked gasoline (Tube-and-Tank process, temperature from 900° to 1000°F at 750 lbs/sq in pressure) in a column corresponding to 115 theoretical plates, into fractions boiling mostly in the range of the principal normal and isoparaffins. The unsaturation of each fraction was determined by bromine numbers. The results are summarized in Table 107. As previously mentioned, the fractions contain not only the hydrocarbons indicated but other hydrocarbons boiling in the range specified in the table.

Table 107. Composition of Butane-Free Cracked Gasoline.

Fraction	Boiling range, ($^{\circ}\text{F}$)	volume % with reference to Gasoline		Volume % of Unsaturates
		Saturates	Unsaturates	
Isopentane	70-85	2.35	1.70	42
<i>n</i> -Pentane	85-100	4.56	2.55	36
Cyclopentane	100-130	0.87	0.97	53
	130-150	2.10	1.90	47
<i>n</i> -Hexane	150-160	3.90	1.90	33
Isoheptanes	160-200	6.20	3.50	36
<i>n</i> -Heptane	200-215	6.80	2.60	28
Octanes	215-260	15.30	5.20	25
Heavier		30.10*	7.50*	20
Total		72.18	27.82	

*Calculated from the total percentage of this fraction 37.6, assuming the relative proportion of unsaturates to be 20 per cent.

The percentage of isopentane, normal pentane, and pentenes should be close to that of the saturated and unsaturated hydrocarbons in the first three fractions. In addition, the authors evaluated the percentage of cyclopentane in the $100\text{--}130^{\circ}\text{F}$ fraction and found approximately 33 per cent. Thus the percentage of some individual hydrocarbons in the cracked naphtha is as follows:

isopentane	2.35 per cent by volume
<i>n</i> -pentane	4.56 " " " "
pentenes	4.25 " " " "
cyclopentane	0.54 " " " "

Frey *et al.*^{14a} give the following composition of the C_5 cracked (non-catalytic pressure cracking) fraction:

Tertiary pentenes	16 per cent
1-Pentene	11 " "
2-Pentenes	20 " "
Pentanes (<i>n</i> and iso)	53 " "

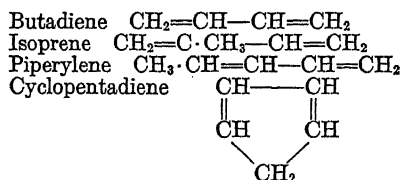
Bates, Kurtz, Rose, and Mills² fractionated the hexane fraction of a thermally cracked gasoline and identified the following isomers:

<i>n</i> -Hexane	63 per cent of hexane fraction
2-Methylpentane	18 " " " " "
3-Methylpentane	16 " " " " "
2,3-Dimethylbutane	3 " " " " "

Thus normal pentane and normal hexane predominate over the corresponding isomeric paraffins in thermally cracked gasolines. Apparently this conclusion on the predominancy of normal and slightly branched structures is true of other paraffins in these gasolines.

By fractionation of a cracked gasoline produced from a Russian kerosene (Cross process), Brame and Hunter⁷ isolated the following hydrocarbons which, however, were not purified: methylcyclopentane, cyclohexane, dimethylcyclopentanes, and methylcyclohexane. Cyclopentane was not detected. Bates *et al.* found only a small amount of cyclopentane in another thermal-cracked gasoline. It is of interest that the content of cyclopentane is small in both straight-run and thermally cracked gasolines, whereas the content of other naphthenes, including cyclohexane and various derivatives of cyclopentane and cyclohexane, is much greater.

The unsaturated olefins in cracked gasolines are mostly open-chain monoölefins. According to Tongberg, Nickels, Lawrosky and Fenske,⁴⁵ 6,7, and 8 carbon-atom olefins predominate in a Pennsylvania Dubbs-cracked gasoline. According to Brame and Hunter,⁷ cyclic olefins occur mostly in the middle boiling range from 90°C (194°F) to 120°C (248°F). Diolefins are present in the low-boiling fractions of cracked gasolines. The proportion of these in mixed phase-cracked gasolines does not exceed 0.1 per cent of the total gasoline, and is much higher in vapor phase-cracked gasolines, amounting to 1 per cent or more (compare page 29). Birch and Scott⁹ removed the diolefins in a vapor phase-cracked gasoline by reaction with maleic anhydride. The following diolefins were separated and identified:



Martin, Gruse and Lowy²⁸ found that the narrow fractions of a vapor phase-cracked gasoline forming very large amounts of gum corresponded to the boiling ranges: 73.9-79.4°C, 101.7-107.2°C, and 123.9-129.4°C. The following diolefins boil in the same boiling ranges: methylpentadienes (74-77°C), cyclohexadienes (78.5-80.5°C), methylcyclohexadienes (108-110°C), heptadiene (107°C), methylhexadiene (107-109°C), dimethylhexadiene (127°C), and dimethylcyclohexadiene (130°C).

In addition to diolefins, vapor phase-cracked gasolines may contain a small amount of styrene and indene. At very high cracking temperatures the content of these hydrocarbons in the cracked products may be

appreciable. Birch and Hague⁴ investigated the composition of "benzol" produced from Persian natural gas at 850°C. The content of pure benzene was close to 75 per cent. In addition to butadiene and cyclopentadiene, the benzol contained approximately 5 per cent styrene and 2 per cent indene.

The formation of diolefins in cracking may be considerable at high temperatures and low pressures, or in the presence of inert gases which prevent the interaction between the diolefins formed and other hydrocarbons. Tropsch, Thomas, Egloff and Morrell⁴⁷ cracked a Pennsylvania gas oil at 950°C and 175 mm pressure for 0.05 second and produced 6.6 per cent butadiene, 3.1 per cent pentadiene, and 7.2 per cent higher conjugated dienes with reference to the oil decomposed.

Catalytically cracked gasolines have a larger percentage of aromatics than do those which are thermally cracked. The average proportion of benzene in the former is about 1 per cent, of toluene 5 per cent, and of xylenes about 10 per cent with reference to the total gasoline (E.P. 350°F).

The paraffin hydrocarbons of catalytically cracked gasolines (Houdry process) were studied by Bates, Kurtz, Rose and Mills.² A typical analysis of light ends of an unstabilized Houdry gasoline by the Podbielniak distillation process gives the following results:

<i>n</i> -Butane	2.3 per cent	<i>n</i> -Pentane	1.3 per cent
Isobutane	10.9 " "	Isopentane	10.3 " "
<i>n</i> -Butene	5.9 " "	Total pentenes	7.3 " "
Isobutene	1.7 " "	C ₆ and heavier	60.3 " "

The high percentage of isobutane and isopentane should be pointed out. The higher paraffinic fractions, C₆ and C₇, were investigated by fractionation of gasolines freed from unsaturates and aromatics, and by analysis of the fractions by the refractive intercept method. The distribution of various hexanes in the hexane cut is as follows:

<i>n</i> -Hexane	9 per cent
2-Methylpentane	48 " "
3-Methylpentane	27 " "
2,3-Dimethylbutane	13 " "
2,2-Dimethylbutane	3 " "

The investigation of C₇-paraffinic fraction was more difficult and the complete separation of all isomers was impossible. The following results were obtained:

Hydrocarbon	Boiling range (°C)	Percentage
2,2-Dimethylpentane	76- 78	6
2,4-Dimethylpentane		
3,3-Dimethylpentane		
2,2,3-Trimethylbutane		
2,3-Dimethylpentane	88- 95	89
2-Methylhexane		
3-Methylhexane		
3-Ethylpentane		
<i>n</i> -Heptane	95-101	5
2,2,4-Trimethylpentane		

The composition of C_6 and C_7 paraffinic fractions also shows that the branched paraffins predominate over normal hydrocarbons, and also that isomers with a moderate degree of branching predominate over those that are highly branched.

Ardern, Newton and Barcus¹ studied the chemical composition of catalytically cracked gasolines from a Coastal crude versus temperature, space rate and distillation range of cuts. The content of olefins and aromatics depends largely on the above factors, while the distribution of paraffins between iso and normal structure did not vary appreciably with charging stock or cracking conditions. The average weight ratios of iso to total paraffins were:

Isobutane/total butanes	0.807
Isopentane/total pentanes	0.935
Isohexanes/total hexanes	0.973

The hexane isomers are mostly 2-methyl and also 3-methyl pentanes, i.e., low branched isomers, as has been found by other workers.

The properties of cracked gasolines closely follow their chemical composition. The percentage of branched paraffins and aromatics predetermines the octane number of cracked gasolines. Thus catalytically cracked gasolines or aromatic gasolines of the high-temperature processes have high octane numbers. The lead-susceptibility of such gasolines, however, is quite different, being satisfactory for catalytically cracked gasolines and poor for aromatic gasolines. The stability depends upon the content of unsaturates, as well as upon their kind. It should be kept in mind that monoölefins are comparatively stable, whereas cyclic olefins and particularly diolefins, aliphatic and cyclic, are very unstable (Flood *et al.*¹⁴) and easily oxidized, forming various oxygen compounds including the so-called gum. The average properties of various cracked gasolines are summarized in Table 108.

Table 108. Properties of Cracked Gasolines (E.P. 400°F).

Gasoline	Percentage of				Spec gr 60°/60°F	Octane No., MM	-Octane 1 cc	No. with 2 cc	TEL- 3 cc
	Aro- matics	Un- saturates	Naph- thenes	Par- affins					
Mixed phase-cracked	6	32	16	46	0.740	67	74	77	79
Vapor phase-cracked	18	45	20	17	0.770	78	82	84	85
Catalytically cracked	18	18	20	44	0.765	78	84	87	89
Thermally re-formed	10	35	15	40	0.750	70	75	77	78
Polyformed	20				0.765	74	77.5	80	81.5

Hydrogenation Gasolines

Hydrogenated gasolines differ from cracked gasolines in that they contain either a very small proportion of unsaturates, or none at all. Table 109 gives some data on their chemical composition.

Table 109. Chemical Composition of Hydrogenation Gasolines.

Charging Stock	Percentage by Weight			
	Aromatics	Unsaturates	Naphthenes	Paraffins
Paraffinic gas oil	5	10	22	63
Naphthenic gas oil	6	1	52	41

The first item of Table 109 is a hydrogenation gasoline produced by a non-catalytic process from a paraffinic gas oil; it contains a small percentage of olefins and a large proportion of paraffins. The second gasoline is produced by a commercial catalytic process from a naphthenic gas oil; it is almost entirely saturated and is rich in naphthenes and paraffins. The percentage of aromatics is low in both. Such a composition is characteristic of hydrogenation gasolines made under moderate temperature conditions, particularly in the presence of very active hydrogenation catalysts.

The fractional composition of a hydrogenation gasoline (the first example of Table 109) is given as follows:

Fraction (°C)	Percentage by weight			
	Aromatics	Unsaturates	Naphthenes	Paraffins
Below 60	0	10	0	90
60-95	6.1	8.9	22.9	62.1
95-122	3.0	11.3	29.1	56.6
122-150	5.5	11.3	29.1	54.1
150-200	10.3	9.3	29.1	56.3

It should be kept in mind that, in the presence of highly active catalysts and at moderate temperatures, aromatic hydrocarbons are hydrogenated into cyclohexanes; and also that the latter can be converted into paraffins by opening the ring. Such gasolines are rich in paraffins and poor in aromatics. Hall and Cawley¹⁶ showed that the chemical composition of hydrogenated gasolines from the same charging stock is strongly affected by the catalyst. The data of Table 110 illustrate the effect of highly active pelleted molybdenum sulfide as catalyst and the less active supported catalyst on the chemical composition of hydrogenation gasolines.

Table 110. Chemical Composition of Hydrogenation Gasolines from Low-temperature Tar in the Presence of Molybdenum Sulfide.

	Supported Catalyst (% by weight)	Pelleted Catalyst
Aromatics	27	2
Naphthenes	66	50
Paraffins	7	48

As in the case of cracking, hydrogenation gasolines may be highly aromatic, if they are produced at temperatures in the range 500-550°C. Less active hydrogenation catalysts are used under these conditions. The specific gravity of such gasolines may be 0.800 or more, and the content of aromatic hydrocarbons up to 50 per cent. At high temperatures of hydrogenation (above 500°C) benzene and its derivatives

are not hydrogenated, even under comparatively high hydrogen pressures. On the contrary, the derivatives of cyclohexane may be dehydrogenated into benzene hydrocarbons under these conditions. The presence of hydrogen only prevents the condensation reactions of aromatic hydrocarbons, which lead to the formation of tars and carbon.

Highly aromatic hydrogenation "safety" fuels and solvent naphthas have been discussed by Byrne, Gohr and Haslam⁹ and by Sweeney and Tilton.⁴⁰

In accordance with the chemical composition of hydrogenation gasolines, the octane number varies in a broad range. Highly paraffinic hydrogenation gasolines, produced over very active catalysts under moderate temperature conditions, have a low octane number (about 60, Motor Method). Highly naphthenic hydrogenation gasolines, produced from naphthenic selective stocks under moderate temperature conditions, may have octane numbers of from 70 to 75. High-temperature hydrogenation gives aromatic gasolines of octane number above 80.

All hydrogenation gasolines are poor in sulfur compounds due to the removal of sulfur as hydrogen sulfide in the process of hydrogenation. The content of sulfur in hydrogenation gasolines usually does not exceed 0.01 per cent, even from charging stocks rich in sulfur.

Synthetic Gas Oils

Synthetic kerosenes and gas oils are obtained as by-products in almost all synthetic processes, such as cracking, hydrogenation, polymerization, etc. Cracked gas oil or recycle stock is an intermediate product of cracking, commonly used for repeated cracking or recycling to obtain the maximum yield of cracked gasoline. Hydrogenation recycle stock is used for the same purpose. It is understood that recycle stocks can also be withdrawn from the process and used as common gas oils, furnace oils, etc. Recycle stocks are obtained in the fractionating equipment of cracking units, mostly in fractionating and flash towers. Fractionating towers separate these stocks from cracked gasoline or naphtha, whereas flash towers separate them from tar or final residuum, which is withdrawn from cracking. Thus recycle stocks from flash towers have a higher boiling range and are more aromatic than those from fractionating towers.

The boiling ranges of recycle stocks may differ, depending on the general scheme of cracking. In non-selective cracking the boiling range of recycle stock is wide, from 150°C (302°F) to 400°C (752°F) or higher. Various fractions of recycle stock may be separated in selective cracking; a light recycle fraction, being cracked under more severe conditions, has a comparatively low end point (about 550 to 600°F).

Recycle stocks differ very substantially from straight-run distillates of the same boiling range because of a high content of unsaturates and aromatics. The content of unsaturates in recycle stocks produced in pressure cracking is usually close to 20 per cent and is considerably less

than in cracked gasolines. Table 111 contains comparative data on the properties of a straight-run distillate and a moderately cracked recycle stock produced from the same mixed-base crude.

Table 111. Properties of Straight-run and Recycle Distillates from Grosny Mixed Base Crude.

	Total Unsat- urates and Aromatics (%)	Sp Gr at 15°C	A.P.I. Gravity	Aniline Point (°C)	Iodine No.	Refractive Index
Straight-run	16	0.806	44.1	68.6	0.35	1.4599
Recycle	36	0.819	41.3	56.4	61.4	1.4677
A.S.T.M. Distillation						
	Flash M.P. (°F)	I.B.P. (°F)	10% (°F)	50% (°F)	90% (°F)	Viscosity at 20°C
Straight-run	144	369	390	439	540	0.01847
Recycle	146	378	414	450	538	0.01864

It will be seen from these data that the two distillates are very similar with reference to the boiling range. On the contrary, the difference in chemical composition is very marked. The recycle stock contains a larger percentage of aromatics and particularly of unsaturates, manifested in high specific gravity, refractive index, iodine number and low aniline point.

Table 112 gives the chemical composition of recycle stocks boiling from 200 to 300°C (392 to 572°F). These were treated with fuming sulfuric acid on a volume for volume basis to remove unsaturates and aromatics. After washing and neutralization, the treated recycle stocks were redistilled up to the end point of the original recycle stocks. The percentage of paraffins and naphthenes was approximately evaluated on the basis of aniline points of the treated products, assuming the aniline factor equal to 5 for gas-oil fractions, according to Carpenter (page 100).

It may be seen from Table 112 that the chemical composition of recycle stocks gives a very clear indication of the nature of the original product. Thus paraffin wax produces a recycle stock containing 55-58 per cent paraffins, and naphthenic and asphaltic stocks give recycle oils containing from 30 to 55 per cent naphthenes. Recycle stocks produced in vapor-phase cracking are much more unsaturated and aromatic than the above stocks formed in pressure cracking.

Few individual hydrocarbons, such as naphthalene and methyl and dimethyl naphthalenes, were isolated from recycle stocks. The content of these aromatic hydrocarbons in recycle stocks depends on the charging stock and mainly on the temperature-time conditions of the process; it may be appreciable in gas oils produced from naphthenic stocks in vapor-phase cracking and may amount to 10 per cent or more of the total. The recycle stocks produced in catalytic cracking are more saturated and more aromatic than those obtained by thermal cracking.

The specific gravity of catalytic recycle stocks varies from 0.875 for paraffin- and mixed-base charging gas oils to 0.915 for naphthenic and

Table 112. Chemical Composition of Recycle Stocks.

Cracking Stock	Cracking Conditions		Recycle Stock				Chemical Composition Aromatic and Unsat- rated Hydro- carbons (%)		Naph- thene Hydro- carbons (%)		Par- affin Hydro- carbons (%)	
			Before Fuming H ₂ SO ₄ Treatment	After Fuming Aniline Point (°C)	Sp Gr @ 15°C	Sp Gr @ 15°C						
			Temp (°C)	Press (atm)	Dura- tion (min)	Point (°C)						
Grozny paraffin distillate	400	5	303	0.840	59.0	80.2	26	34	40		
Grozny paraffin distillate	425	5	63	0.831	60.1	0.795	82.0	32	25	43		
Grozny paraffin distillate	425	10	63	0.838	58.7	0.795	79.9	31	32	37		
Paraffin wax	450	10	12	0.782	75.2	0.771	85.5	28	14	58		
Paraffin wax	450	10	32	0.783	0.773	85.9	34	11	55		
Medicinal Vaseline oil	450	10	12	0.843	0.810	77.0	45	34	21		
Grozny asphalt base gas oil distillate	450	10	12	0.862	0.823	79.6	40	29	31		
Grozny spindle-oil distillate	450	10	12	0.862	0.812	77.3	45	33	22		
Grozny asphalt-base engine oil distillate	450	10	12	0.862	0.814	77.1	45	34	21		
Grozny asphalt-base cylinder oil distillate	450	10	12	0.850	0.807	77.4	41	35	24		
Grozny asphalt-base fuel oil	450	10	12	0.852	0.807	77.7	48	30	22		
Katuga crude oil	450	10	12	0.868	43.5	0.830	71.4	38	55	7		
Baku engine oil	450	10	12	0.849	0.808	77.1	40	37	23		
Grozny mixed-base fuel oil	450	10	12	0.833	0.795	82.2	31	25	44		

asphaltic-base charging gas oils; this indicates a varied degree of aromaticity.

Hydrogenation recycle stocks are completely saturated and close to straight-run gas oils. They are almost sulfur-free. The aromaticity of such recycle stocks depends upon the temperature conditions of the process. Vlughter, Waterman and van Westen⁴⁸ hydrogenated non-destructively various gas oils (Diesel fuels) with the following results:

	Straight-run				Cracked	
	Origin	Hydrog	Origin	Hydrog	Origin	Hydrog
D ₁ ²⁰	0.9004	0.8630	0.8801	0.8320	0.8632	0.8192
Aniline point	42.0	63.6	63.5	80.6	52.0	78.4
Cetene no.	37	49	53	68	61	79
Cetane no.	32	43	46	59	53	69
% by wt of olefins	16	..
% by wt of arom. rings	28	7	20	3	20	2
% by wt of naphth. rings	30	45	17	29	13	26
% by wt of paraff. side chains	42	48	63	68	67	72

Synthetic High-Boiling Fractions

Synthetic high-boiling fractions, like synthetic gas oils, are formed as by-products in such processes as cracking, hydrogenation, etc. They may also be obtained as main products, as, for instance, polymerized lubricating oils, synthetic resins, and similar materials. The chemical composition of synthetic high-boiling fractions and products varies in a broad range depending on the original stock and the character of the treatment.

High-Boiling Fractions Produced by Cracking.—The cracking process produces highly aromatic high-boiling fractions, distilling above 350–400°C (662–752°F) under atmospheric pressure.

The properties of high-boiling cracked distillates versus cracking conditions were studied by Sachanen and Bestougeff.³⁵ A Balachany fuel oil of specific gravity 0.908 was cracked at 425°C (797°F) and 15 atmospheres' pressure. The duration of cracking varied within a wide range, from 30 minutes to 6 hours. The results are given in Table 113.

Table 113. Cracking Balachany Fuel.
Cracking Temperature 425°C (797°F), Pressure 15 atm

Time	Yields (% by wt)				
	Gas + Loss	Gasoline up to 392°F	Recycle Stock 392–572°F	Residuum	Coke
32 min	5.1	12.2	21.1	61.6	0.0
1 hour 32 "	6.7	28.6	23.4	41.0	0.3
3 " 02 "	11.3	36.8	22.0	28.6	1.3
6 " 02 "	14.7	52.3	13.1	7.9	12.0

The residues obtained were distilled in high vacuum, and the boiling temperatures under vacuum were converted to atmospheric pressure according to the equation of Ramsay and Young and the boiling curve of normal octane. The results of distillation and the properties of fractions are given in Tables 114–117.

Table 114. Vacuum Distillation Cracked Residuum from Balachany Fuel Oil.
Duration of Cracking 32 Minutes.

The cracked residuum had a specific gravity of 0.927, pour point below -20°C , flash point 184°C , Saybolt viscosity 240 at 122°F . The residuum amounts to 61.6 per cent of the original fuel oil.

Fraction No.	—Boiling Temperature—		Mercury Pressure (mm)	% Over	Sp Gr at 15°C	Pour Test ($^{\circ}\text{C}$)	Flash Point ($^{\circ}\text{C}$)	Saybolt Viscosity at 122°F
	Atmospheric Pressure ($^{\circ}\text{C}$)	During Distillation ($^{\circ}\text{C}$)						
1	290-339	142-178	11	9.1	0.882	below -20	143	41
2	339-366	178-205	11 -14	7.6	0.891	below -20	159	48
3	366-394	205-226	14	8.0	0.897	-15	176	58
4	394-408	226-239	14 -15.5	8.3	0.904	-5.5	191	70
5	408-427	239-248	15.5-13	7.6	0.913	$+2$	205	96
6	427-449	248-267	13 -14	7.4	0.918	7	216	144
7	449-474	267-288	14 -15	7.6	0.924	9	228	235
8	474-492	288-303	15 -16	7.5	0.928	15	237	330
9	492-536	303-325	16 -10.5	7.7	0.930	21	270	550
Bottoms				27.3	0.979			fluid
Losses				1.9				

Table 115. Vacuum Distillation of Cracked Residuum from Balachany Fuel Oil.
Duration of Cracking 1 Hour, 32 Minutes.

The cracked residuum had a specific gravity of 0.966, pour point below -20°C , flash point 167°C , Saybolt viscosity 280 at 122°F . The residuum amounts to 41 per cent of the original fuel oil.

Fraction No.	—Boiling Temperature—		Mercury Pressure (mm)	% Over	Sp Gr at 15°C	Pour Test ($^{\circ}\text{C}$)	Flash Point ($^{\circ}\text{C}$)	Saybolt Viscosity at 122°F
	Atmospheric Pressure ($^{\circ}\text{C}$)	During Distillation ($^{\circ}\text{C}$)						
1	297-336	142.5-170.5	9	8.4	0.896	below -20	137	40
2	336-361	170.5-189	9	8.0	0.903	-20	151	44
3	361-378	189 -202	9	7.7	0.911	-14	164	50
4	378-386	202 -236	9 -20	8.4	0.923	-6	177	61
5	386-400	236 -248	20	7.4	0.934	-0.5	191	76
6	400-432	248 -248	20 -11.5	7.8	0.941	$+2$	205	100
7	432-451	248 -262	11.5	7.7	0.948	$+12$	217	165
8	451-480	262 -282	11.5-11	7.9	0.958	$+18$	231	235
9	480-519	282 -310	11 -10.5	7.4	0.970	$+20$	246	680
10	519-551	310 -332	10.5-10	7.7	0.984	$+18$	257	126
Bottoms				19.9	1.11			at 212°F
Losses				1.6				

The progressive change in the chemical composition of cracked distillates versus time of cracking is first noticed in the specific gravity. In addition to high specific gravity, the heavy cracked fractions become less viscous. However, the properties of cracked fractions in the first three experiments (time from 32 minutes to 3 hours 2 minutes) remain to a certain degree similar to those of straight-run distillates. Under the most severe conditions employed (6 hours 2 minutes), the cracked fractions completely lose their petroleum character. They consist mostly of solid aromatic hydrocarbons. A more complete information on the hydrocarbons in high-boiling cracked distillates was obtained as a result of fur-

Table 116. Vacuum Distillation of Cracked Residuum from Balachany Fuel Oil. Duration of Cracking 3 Hours and 2 Minutes.

The cracked residuum had a specific gravity of 1.018, pour point of -13°C , flash point of 168°C , Saybolt viscosity 605 at 122°F . The residuum amounted to 28.7 per cent of the original fuel oil.

Fraction No.	-Boiling Temperature- At		Mercury Pressure (mm)	% Over	Sp Gr at (15°C)	Pour Test $(^{\circ}\text{C})$	Flash Point $(^{\circ}\text{C})$	Saybolt Viscosity at 122°F
	Atmospheric Pressure $(^{\circ}\text{C})$	During Distillation $(^{\circ}\text{C})$						
1	311-338	150-169	8 -7	8.5	0.920	below -20	136	37
2	338-358	169-180	7 -6.5	8.2	0.932	-16	159	44
3	358-376	180-192	6.5	8.1	0.959	-14	171	52
4	376-392	192-203	6.5	8.8	0.959	- 7	180	60
5	392-413	203-218	6.5	8.0	0.969	+ 3	191	80
6	413-435	218-233	6.5	7.7	0.980	+ 9	202	130
7	435-470	233-256	6.5-6	7.8	0.995	+14	215	285
8	470-524	256-295	6.0	7.7	1.02	+20	231	78
9	524-568	295-326	6.0	8.1	1.05	+10	246	at 212°F
10	568-588	326-340	6.0	6.6	1.08			172
Bottoms				20.0	1.19			*
Losses				0.5				†

*Semi-solid melting point by Kremer-Sarnow 25°C

†Semi-solid melting point by Kremer-Sarnow 155°C

Table 117. Vacuum Distillation of Cracked Residuum from Balachany Fuel Oil. Duration of Cracking 6 Hours and 2 Minutes.

The cracked residuum had a specific gravity of 1.12. The residuum amounted to 7.9 of the original fuel oil.

Fraction No.	-Boiling Temperature- at		Mercury Pressure (mm)	% Over	Sp Gr at (15°C)	Pour Test $(^{\circ}\text{C})$	Saybolt Viscosity at 122°F
	Atmospheric Pressure $(^{\circ}\text{C})$	During Distillation $(^{\circ}\text{C})$					
1 and 2	280-354	139-194	13	16.5	0.995		40
3 and 4	354-416	194-235	13 -11	21.5	1.058	separation of crystals	64
5 and 6	416-546	235-329	11 -10.5	18.3	1.11	separation of crystals	
7 and 8	546-554	329-343	10.5-13	14.3	1.14	separation of crystals	solid
Bottoms				29.1	1.23		
Losses				0.3			

Table 118. Molecular Weights, Ultimate Analysis and Formulas of Cracked Fractions Obtained in Cracking at 425°C (797°F) for 3 Hours 2 Minutes.

No. of Fraction	Boiling Temp $(^{\circ}\text{C})$	Sp Gr at 15°C	Molecular Weight	—Ultimate Analysis—			Formula	Series
				Hydrogen	Carbon	Total		
1	311-338	0.920	211					
2	338-358	0.932	229	11.62	88.30	99.92	$\text{C}_{17}\text{H}_{26}$	$\text{C}_n\text{H}_{2n-8}$
3	358-376	0.959	245					
4	376-392	0.959	260	11.04	88.09	99.13	$\text{C}_{19}\text{H}_{28}$	$\text{C}_n\text{H}_{2n-10}$
5	392-413	0.969	246					
6	413-435	0.980	289	10.64	88.98	99.62	$\text{C}_{22}\text{H}_{30}$	$\text{C}_n\text{H}_{2n-10}$
7	435-470	0.995	298					
8	470-524	1.02	317	9.62	88.68	98.30	$\text{C}_{23}\text{H}_{30}$	$\text{C}_n\text{H}_{2n-10}$
9	524-568	1.05	370	9.59	89.74	99.33	$\text{C}_{28}\text{H}_{36}$	$\text{C}_n\text{H}_{2n-20}$
10	568-588	1.08	370					

ther investigation. Tables 118 and 119 give the data on the molecular weight, ultimate analysis and average formulas of the fractions corresponding to Tables 116 and 117, *i.e.*, to the cracking conditions 3 hours and 6 hours at 425°C. The molecular weights were determined in benzene solutions. In the calculations of formulas the content of oxygen was not taken into consideration due to the comparatively small amount present in the fractions.

Table 119. Molecular Weights, Ultimate Analysis and Formulas of Cracked Fractions Obtained in Cracking at 425°C (797°F) for 6 Hours, 2 Minutes.

No. of Fraction	Boiling Temp (°C)	Sp Gr at 15°C	Molecular Weight	—Ultimate Analysis—			Formula	Series
				Hydrogen	Carbon	Total		
1-2	280-354	0.995	199	9.36	90.28	99.63	$C_{15}H_{18}$	C_nH_{2n-12}
3-4	354-416	1.058	220	7.94	91.50	99.44	$C_{17}H_{18}$	C_nH_{2n-16}
5-6	416-546	1.11	252	7.17	91.15	98.32	$C_{19}H_{18}$	C_nH_{2n-20}
7-8	546-554	1.14	294	6.85	92.29	99.14	$C_{23}H_{20}$	C_nH_{2n-28}

The aromatization of hydrocarbons is almost complete after cracking under more severe conditions. For instance, the chemical composition of cracked oils obtained after even three hours' cracking of Balachany fuel oil corresponds to that of aromatic hydrocarbons, and only the lighter gas oil fractions can contain hydroaromatic compounds which are derivatives of Tetralin. The dehydrogenation of naphthenes is very easily carried out and is completed before the hydrocarbon has lost all its side chains, due to the fact that after the long chains have been split up, the splitting up of short chains, particularly those of methyl groups is carried out with more difficulty.

The crystalline fractions obtained after 6 hours' cracking are purely aromatic. The larger part of the crystals separated in one of the fractions had a melting point of 201°C, which is close to the melting point of 202 to 203°C for 1,3-dimethylantracene. Analysis of the crystals revealed the composition to be 93.10 per cent carbon and 6.66 per cent hydrogen, as compared with 93.16 per cent and 6.84 per cent of carbon and hydrogen, respectively, in dimethylantracene.

The small amount of fractions left after the investigation did not permit a more complete investigation of the solid compounds present. Therefore only their melting points could be determined after twice recrystallizing from alcohol. Due to the fact that most of the crystals obtained were probably a mixture of isomers, their melting temperatures between 190 and 230°C could be of only informational value. The ultimate analysis and the melting points indicate that these crystalline hydrocarbons are composed principally of substituted anthracenes or phenanthrenes.

Orlov, Protyanova and Flegontov³² studied the chemical composition of a residuum from high-temperature cracking of liquid petroleum products at 700-800°C (1292-1472°F). The following compounds were isolated: naphthalene, α - and β -methylnaphthalene, mixture of dimethylnaphthalenes, acenaphthene, anthracene and phenanthrene. Correspond-

ing to the high temperature of the process, the residuum contained a considerable amount of non-alkylated aromatic hydrocarbons, as products of complete dealkylation and dehydrogenation.

Table 120. Vacuum Distillation of Cross Cracked Residuum from Mid-Continent Gas Oil.*

No. of Fraction	% by Vol	Temp (°F)	Gravity A.P.I.	Flash Point (°F)	Pour Point (°F)	—Viscosity at— 100°F 210°F		Aniline Point (°F)
Res.	100			250	25		55	
1	10	100-240	24.0	150	-30	35.2		54.3
2	10	240-275	20.5	235	0	41.4		57.0
3	10	275-315	18.2	295	20	53.0		57.5
4	10	315-345	15.6	315	45	74.4		65.8
5	10	345-390	14.1	350	65		39.8	100.7
6	10	390-450	13.3	410	85		49.0	
7	10	450-490	13.3	445	100		64.8	
Bottoms	30							

*The pressure was 2 mm Hg for all.

The heavy distillates of commercial cracked residues closely correspond to those of Tables 115 and 116, or to the temperature-time factors 425°C (797°F) for 92 minutes, and 425°C for 182 minutes. The specific gravities and aromaticity of the distillates may be higher or lower depending upon the charging stock. Table 120 contains the data on the distillates of a Cross residuum. The content of unsaturates and aromatics absorbed by concentrated sulfuric acid is about 50 per cent for the first five fractions and about 70 per cent for the last two fractions. The degree of aromatization of cracked fractions of the Cross-cracked residuum is close to that of the above experiment at 425°C for 182 minutes (Table 116). The heavy distillates of reforming or vapor phase-cracked residues are highly aromatic because of the drastic conditions of the processes in question.

High-Boiling Fractions Produced by Hydrogenation

High-boiling fractions produced by hydrogenation at moderate temperatures and in the presence of highly active catalysts differ very substantially from those produced by cracking described in the previous section. As might be expected, the aromaticity of the hydrogenated high-boiling fractions is low and the saturation is complete. As a result, they consist predominantly of naphthenic and paraffinic hydrocarbons or of naphthenic hydrocarbons and paraffinic side chains. Aromatic rings may be present in a minor proportion.

Hydrogenated high-boiling fractions are viscous and possess lubricating properties. Their viscosity index is usually high and exceeds that of the corresponding virgin fractions. The content of sulfur is low, as in other hydrogenated products. In general, the hydrocarbons of hydrogenated high-boiling fractions are very close to those present in straight-run lubricating oils of the Pennsylvania type.

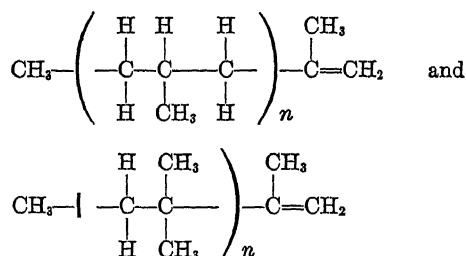
According to Haslam and Russell,¹⁷ a Winkler lubricating distillate

having a viscosity index of 32 and a Conradson carbon of 0.410 per cent produced a hydrogenated lubricant of viscosity index 83 and Conradson carbon 0.015 per cent; another Mid-Continent lubricating oil, viscosity index 72 and Conradson carbon 3.31 per cent, produced a hydrogenated oil with a viscosity index of 101 and a Conradson carbon of 0.13 per cent. It should be mentioned, however, that such an improvement in the properties is accompanied by a substantial decrease in viscosity.

Polymerized High-boiling Fractions

The catalytic polymerization of olefins under certain conditions produces synthetic high-boiling hydrocarbons. The molecular weight of these hydrocarbons, as well as the structure, depends upon the olefins to be polymerized, the temperature and the catalyst used. The polymerized hydrocarbons may be pure olefins (polyolefins) or olefins and other hydrocarbons, including paraffins, naphthenes and aromatics, as a result of various secondary reactions.

The tentative and schematic structure of the synthetic lubricating oils from normal and isobutene would be as follows, on the assumption that the oil is a true olefinic polymer:



respectively. The number of carbon atoms in the polymer lubricating oil is upwards of 25, depending on the viscosity.

The structure of synthetic lubricating oils with naphthenic or aromatic rings (as a result of secondary reactions) is entirely unknown. It may be postulated that some of the carbon atoms of the chains are isomerized or condensed, for instance, into a hydroaromatic or aromatic ring, and that the rest of the chain becomes a side chain of the ring formed.

The effect of catalysts on polymerization is very conspicuous. As discussed above, the polymerization of low molecular weight olefins, such as propene or butenes, in the presence of sulfuric or phosphoric acid produces mostly dimers and trimers, as well as other medium molecular weight hydrocarbons, as a result of secondary reactions. The total synthetic products boil mostly in the range of gasolines. The polymerization of olefins of a higher molecular weight in the presence of the same catalysts also gives mostly dimers and trimers. On the contrary, polymerization of olefins in the presence of aluminum chloride or boron fluo-

ride at room temperature and up to 100°C produces high molecular weight hydrocarbons, including those which boil in the range of lubricating oils and have lubricating properties.

Nash, Stanley and Bowen³⁰ investigated the composition of synthetic lubricating oils produced by catalytic polymerization of ethene with aluminum chloride at room temperature and from 75 to 180°C. The higher the temperature the more cyclic and polycyclic are the hydrocarbons produced. The lubricating oil fractions obtained by polymerization at 150°C, for instance, correspond to the approximate general formula from C_nH_{2n-4} to C_nH_{2n-10} . Such fractions are almost saturated and consist of polynuclear naphthenes. The lubricating oils obtained by polymerization at room temperature differ in properties depending on whether they are produced from the "free" oil (the upper layer) or from the oil combined with aluminum chloride. The first oils consist mainly of saturated hydrocarbons, probably monocyclic naphthenes, and the oils from the lower layer consist partly of unsaturated hydrocarbons, probably olefins.

Sullivan, Voorhees, Neely and Shankland³⁹ obtained lubricating oils from various olefins and olefinic materials in the presence of aluminum chloride at temperatures between 70 and 200°F (21 to 93°C). The reaction time was several hours. The yields and properties of the lubricating oils synthesized are given in Table 121.

It should be pointed out that the properties of polymerized lubricating oils depend largely upon the conditions of polymerization. As the data of Table 121 show, the polymerization of low molecular weight olefins, particularly of ethene, produces lubricating oils of low viscosity index. Hessels, van Krevelen and Waterman¹⁸ found, however, that ethene polymerized over aluminum chloride in the presence of activated nickel on kieselguhr or over aluminum chloride in an autoclave of Hastelloy A steel gives lubricating oils of high viscosity index (up to 107).

Koch and Gilfert²⁴ described the synthesis of polymerized lubricating oils from light ends of Kogasine produced from carbon monoxide and hydrogen (the Fischer-Tropsch process). The fractions boiling between 35 and 125°C, containing from 43 to 75 per cent olefins, were polymerized with 5 per cent of aluminum chloride at 0°C. The yield of lubricating oils was from 37 to 68 per cent. The lubricating oils have an exceptionally low specific gravity of about 0.845 (viscosity up to 6000 S.U. at 50°C) and a high viscosity index.

The composition of lubricating oils produced by the catalytic polymerization of olefins has not been investigated. It is probable, however, that they consist of polyolefins, naphthenes and paraffins, the latter being formed by isomerization and other secondary reactions of primary polyolefins. The oils of low viscosity index consist predominantly of polycyclic naphthenes; those of high viscosity index contain either polyolefins or naphthenic rings with long paraffinic side chains. If the conditions of polymerization are mild and carefully controlled, pure polyolefins can

be formed. The data of Table 122 indicate that the iodine number of such oils corresponds exactly to one double bond.

Table 121. Polymerized Lubricating Oils Produced from Various Olefins and Distillates.

Hydrocarbon or Original Product	Yield (wt %)	API Gravity	—Saybolt Visc. at—		V.I.	Pour test (°F)
			100°F	210°F		
Ethene		18.0	2769	80	-150	
Propene	33.3	33.1	1083	70	20	-10
Butene-1		34.3	1654	92	50	-10
"	46.4		1122	78		
Butene-2	33.3	34.7	1507	81	21	-5
Isobutene	42.0		3706	147	67	
"		32.5	1540	94		
"			868	73		-10
Pentene-1	59.8		1350	94	82	
"		33.2	1180	89		-15
Pentene-2	38.5	32.8	1946	93	27	0
"	53.0		976	68		
3-Methylbutene-1	50.8	34.0	3301	108	0	5
"			938	65		
"			321	50		
2-Methylbutene-1	34.5	33.7	1959	89	11	5
"			998	68		
Trimethylethene		31.0	1476	70	-74	25
"	29.3		367	49		
Hexene-1		34.3	1115	92	91	-25
Octene-1		34.8	905	88	104	-20
Cetene	85	33.9	1774	201	138	45
"		34.8	1187	153		45
"		35.9	717	108		40
Cyclohexene		18.0	2135	85	-27	25
Turpentine		15.8	4750	83	-324	30
Cracked dist. 225-500°F from gas oil	17.9	15.4	3650	86	-172	-15
Cracked dist. 320-420°F from shale oil	19.6	14.5	2430	84	-64	-15
Cracked dist. 300-500°F, M.C. naphtha	50.5	23.6	1500	85	41	5
Cracked dist. to 300°F from oleic acid	48.0	23.4	1420	87	52	-10
Cracked dist. 300-350°F, Penn. gasoline	51.3	26.8	1275	86	63	-5
Cracked dist. 300-500°F, from ozokerite	16.5	26.0	914	85	97	-25
Cracked dist. 300-500°F, from wax	50.0	30.8	835	84	103	-35
Cracked dist. to 428°F, from paraffin wax	45.0	33.1	797	85	109	-10
Cracked dist. 300-500°F, from petroleum wax	55.0	31.3	735	87	118	-35

Hydrogenation of synthetic polymerized lubricating oils may produce purely paraffinic lubricating oils. It is understood that the original polymerized oils must be purely olefinic and free of cyclic hydrocarbons. The paraffinic lubricating oils have a lower specific gravity and refractive index than straight-run lubricating products, even from Pennsylvania crudes. The pour point may be low due to the iso-structure of the paraffins. Lyman and Gardiner²⁶ give the following properties of a polymerized olefinic lubricating oil and the hydrogenated oil produced from the

polymers (Table 122). The original polymerized oil has a distillation range from 475 to 600°F at 10 mm.

Table 122. Properties of Polymerized Lubricating Oil and Hydrogenated Product.

Properties	Polymerized Oil	Same after Hydrogenation
Specific gravity, 60°/60°F	0.8337	0.8192
API gravity	38.2	41.2
Refractive index	1.4675	1.4570
Saybolt viscosity at 100°F	407	185
Molecular weight	391	347
Per cent of carbon	85.7	85.3
Per cent of hydrogen	14.3	14.7
Bromine number (per gram oil)	0.41	0.015
Per cent of unsaturates	100	3.3
Empiric formula	C_nH_{2n}	C_nH_{2n+2}
Type of hydrocarbons	olefins	branched paraffins

No data concerning the structure of isoparaffins of the above lubricating oils are available.

Voltolized oils may be considered as semi-synthetic lubricating oils produced from conventional lubricating oils (sometimes with fatty oils) by the action of silent electrical discharges. The process results in the dehydrogenation and further polymerization of the treated oil. Accordingly, voltolized oils have molecular weights up to 6000 and correspondingly high viscosities. Their general chemical structure should be close to that of the original oils.

Synthetic lubricating oils are not manufactured in the U. S. because of the availability and cheapness of conventional lubricating oils of petroleum origin. Modern methods of refining produce high-grade lubricating oils which are not inferior to synthetic oils. Germany is a producer of voltolized oils and polymerized lubricating oils from the light ends of Kogasine, as has been mentioned above. The volume of this production is unknown.

Synthetic Petroleum Resins

Synthetic resins, being non-volatile, cannot be considered as distillates. They are included, however, in view of the close relationship between them and other synthetic products described above, and in view of purely hydrocarbon composition of the synthetic resins discussed in this chapter.

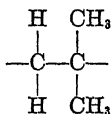
As stated in the previous section, the polymerization of olefins in the presence of aluminum chloride at moderate temperatures yields polymerized products of fairly high molecular weight. Some of the polymerized fractions formed have the molecular weight and properties of lubricating oils. Certain olefins, for instance, isobutene, polymerized in the presence of the same catalyst, at very low temperatures (below -50°C) produce very high molecular weight polymers which have the properties of resins.^{43, 44} The polymerization of conjugated diolefins, alone or in the presence of some modifiers, yields resins which possess rubber-like properties. The resins and rubber produced from ethene, butenes and butadiene

may be considered as of petroleum origin, since these hydrocarbons are obtained either from cracking products or by cracking of specific petroleum hydrocarbons.

This does not mean, however, that these resins and synthetic rubber cannot be produced from other sources than petroleum. Butadiene, for instance, may be synthesized from ethyl alcohol or acetylene. As a matter of fact, the production of butadiene from the last two sources takes place in Russia and Germany on a commercial scale, as well as from ethyl alcohol in this country.

The polymerization of ethene produces polyethenes or polyethylenes of high molecular weight (polythene or alkathene), a very valuable commercial plastic. This plastic has apparently a simple chain structure.

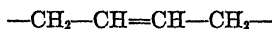
The polymerization of isobutene at very low temperatures and in the presence of very small quantities of such catalysts as aluminum chloride or boron fluoride yields polymers of molecular weight from 20,000 to 400,000. The polymers have the probable chain structure:



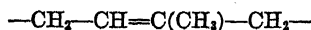
The polymers have one end-double bond in a very large molecule and are practically saturated. The properties of these resins depend upon the molecular weight, varying from soft to very tough consistency. The high molecular weight resins (more than 100,000) have some rubber-like properties. Such resins have been described by Sparks *et al.*^{38, 12} The polymers are colloiddally soluble in petroleum and lubricating oils, which modifies their properties. The viscosity and viscosity index of lubricating oils increase in the presence of such dissolved resins, the extent of this increase depending upon the concentration of the resin. A small percentage, *e.g.*, 1 per cent of the resin or less, is sufficient to increase appreciably the viscosity and viscosity index. A greater proportion of the resin in the oil produces greases and jelly-like structures.

These resins were developed by I. G. Farbenindustrie and Standard Oil Co. of New Jersey and are now used on a large commercial scale for modifying lubricating properties, *e.g.*, Vistanex and Paraton. Paraton is the resin dissolved in an excess (2 or 3 parts) of a neutral lubricating oil.

The polymerization of butadiene-1,3 or its homologs over metallic sodium produces synthetic rubber of the structure



The polymerization of isoprene or methylbutadiene-1,3 yields isoprene synthetic rubber of the structure

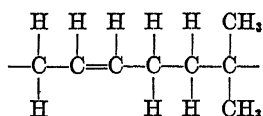


which is close to that of natural rubber. It has been assumed that the process of polymerization is not accompanied by any secondary reactions of rearrangement, which would involve a change in the above structure of the chains.

The possibility that the chains of rubber molecules may have a cyclic structure has been pointed out recently by Zelinsky and Rapoport,⁵¹ who catalytically and destructively hydrogenated rubber, producing a high yield of naphthenes and cycloolefins.

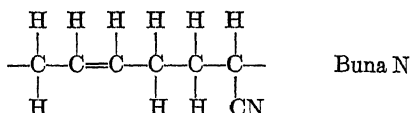
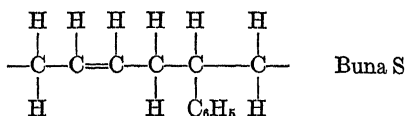
These synthetic butadiene rubbers are rubber-like and can be vulcanized due to the presence of double bonds. The degree of polymerization predetermines their properties; they may have consistency from viscous semi-liquids to solid.²³ Their properties are, however, inferior to those of natural rubber. The processes of manufacturing butadiene rubbers were developed in Germany and Russia, in which countries they are or were used extensively on a commercial scale.

While the polymerization of isobutene does not yield vulcanizable rubber, it has been shown that the conjoint polymerization of isobutene and butadiene or isoprene yields true synthetic rubber.²³ The reaction is carried out at low temperatures (*e.g.*, -50°C) in the presence of a small proportion of aluminum chloride (a small fraction of 1 per cent). The proportion of isobutene is much greater than that of butadiene. Assuming the interpolymerization of one molecule of isobutene and one molecule of butadiene, the structure of the synthetic rubber or Butyl rubber is



It should be kept in mind that the proportion of butadiene in the copolymerization is much less than of isobutene, as has been stated above. As much as 98 per cent of isobutene is polymerized with 2 per cent of butadiene or isoprene. Accordingly, the total unsaturation is much less than indicated by the above formula. The unsaturation of Butyl rubber is also much less than that of natural rubber. Thomas *et al.*⁴² state that the unsaturation of Butyl rubber corresponds to 1-2 per cent of that found in natural rubber; as a result, Butyl rubber is chemically more stable than the natural product. As far as the other properties are concerned, Butyl rubber is inferior to natural. The process has been developed by the Standard Oil Co. of New Jersey.

The inferior qualities of synthetic butadiene rubbers can be considerably improved by the copolymerization of butadiene with such unsaturated compounds as styrene or acrylonitrile, the structure of which also is essentially conjugated. The polymerization of butadiene and styrene or of butadiene and acrylonitrile produces Buna S and Buna N, or Perbunan, respectively of the following structures:



It also has been assumed that one molecule of butadiene is polymerized with one molecule of styrene or acrylonitrile. Actually the proportion of butadiene is much greater than of the modifiers, so that several molecules of butadiene are copolymerized with one molecule of a modifier. Bunas S and N are more saturated than natural rubber due to the partial saturation of double bonds.

The copolymerization of butadiene and styrene or acrylonitrile is carried out by the so-called "emulsion" process. The reaction components, *i.e.*, butadiene and a modifier, are emulsified in a small amount or in an excess of water in the presence of an emulsifier, protective colloid, and polymerization catalyst. The emulsifiers, such as soaps, sulfonates, and protective colloids, such as gelatin or albumen, are used in the proportion of about 5 per cent with respect to the polymer. The polymerizing catalyst is usually an oxidizer (peroxide). The amount of catalyst used is customarily small, less than 1 per cent based on the polymer. Other addition agents are also used.²⁷ The process takes place at room or moderate temperatures from 30 to 60°C and may last 20 hours or more. The latex of the synthetic rubber formed is coagulated by an acid.

Bunas S and N possess rubber-like properties, are superior to other types of the synthetic rubber and, in some instances, to natural rubber. Buna N, for instance, is much less soluble and much less susceptible to swelling in various organic solvents, including petroleum oils, than is natural rubber. Hycar, Chemigum, and Ameripol are commercial names of the synthetic rubber produced by copolymerization of butadiene with the modifiers mentioned above.

Other types of synthetic rubber are of non-petroleum origin and thus are beyond the scope of this volume.

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Chapter 6

Petroleum Wax

Types of Petroleum Wax

Petroleum wax represents solid hydrocarbons, mostly paraffinic, which occur in crude oils, distillates, and residues, and have a "waxy" structure and melting points above 30-35° (86-95°F). The last limitation, however arbitrary, appears to be substantial, since the paraffins of lower melting points, largely represented in gas-oil fractions, are not considered as petroleum wax. Such hydrocarbons are readily dissolved in petroleum fractions even at low temperatures, and cannot be separated by the conventional methods used in the manufacture of petroleum wax. Paraffin wax and other petroleum waxes are produced from comparatively high-boiling fractions, such as heavier gas oils, paraffin distillates and residues. It is understood that the border line between "solid" petroleum wax hydrocarbons and "liquid" paraffins is neither definite nor scientific. Normal eicosane with a melting point of 36.4°C is rather close to this border line.

Highly cracked products may contain such solid hydrocarbons as naphthalene or derivatives of anthracene or phenanthrene, which do not have a waxy structure and thus do not belong to the petroleum waxes. As will be seen later, some petroleum waxes probably have a ring structure, but in any case they possess long paraffinic side chains which are closely related to the so-called waxy structure.

The nomenclature of petroleum waxes is not definite. The name "paraffin wax" is sometimes used as a generic term embracing all solid paraffins and similar hydrocarbons of waxy structure, which are present in crude oils and distillates. The generic term "petroleum wax" used in this volume is preferable. The former term is used in a more specific sense to designate the petroleum wax separated or manufactured from comparatively light petroleum fractions, including gas oil and neutrals. Petroleum ceresin or microcrystalline wax is that separated from residues or petrolatum. Rod wax is formed by spontaneous precipitation from crude oils in sucker rods or in storage; it contains high molecular weight petroleum waxes of the ceresin type.

A wax of the same type is deposited on the walls of tubes used for pumping paraffinic crudes. For instance, the 10-inch pipe line between Grozny and Tuapse has been used to pump highly paraffinic Grozny crude oil with 30 per cent of gasoline and kerosene distillates to be redistilled in the Tuapse refinery. A considerable amount of petroleum wax is deposited on the wall of the pipe line as well as in the storage tanks of

the pumping stations. The pipe line is periodically cleaned by scrapers. Ceresin wax is produced on a commercial scale from the deposit removed from the pipe line and storage tanks.

The properties of paraffin wax and petroleum ceresin are quite different. Paraffin wax crystallizes in large crystals, plates, or needles. It absorbs loosely the oils which can be easily separated by filtration or sweating under appropriate conditions. Petroleum ceresin crystallizes in such small crystals that the earlier investigators attributed an amorphous structure to it. Detection of the crystalline structure in petroleum ceresin under a microscope does not present any difficulties, however. Micro-crystalline wax absorbs or adsorbs oils tenaciously, the separation of which is a much more difficult problem than in the case of paraffin wax.

The properties of paraffin wax, which consists mostly of normal paraffins, as will be seen later, are uniform and do not depend on the origin. Thus, oil-free paraffin waxes, produced from any crude oil, will have the same properties. There is no evidence that the same would be true of petroleum ceresins; it is quite possible that petroleum ceresins of the same melting point will differ to a certain extent in their properties depending upon their origin and structure.

Content of Petroleum Wax in Crude Oils and Other Sources

The content of petroleum wax in crude oils varies within broad limits. The wax content of naphthenic and asphaltic crude oils is usually small, not exceeding 1 per cent, but may be comparatively high in some crudes of these types. Paraffin-base and mixed-base crude oils may contain as much as 10 per cent of petroleum wax. Table 123 gives some data on the petroleum wax content in various crude oils. It should be kept in mind that the figures given in the table have been obtained by different methods and in various laboratories. In some cases the Holde-Engler method with destructive distillation, resulting in a partial cracking of petroleum wax, was employed (Chapter 2). Thus, the data are not quite comparable and in some cases may be appreciably lower than the actual percentage of petroleum wax.

Straight-run distillation of paraffin-base and mixed-base crude oils gives paraffin distillates usually boiling from 150° (302°F) to 300° (572°F) at 10 mm pressure and containing from 10 to 25 per cent of paraffin waxes, including those of low melting point. The slack wax, obtained by filtration of chilled paraffin distillate (eventually in a solvent), contains 60 per cent or more of paraffin wax. The scale wax is obtained from the slack wax by sweating or by crystallization from a solvent and contains upwards of 97 per cent of paraffin wax.

Straight-run or "steam refined" residues (long residues or cylinder stocks) of paraffin-base or mixed-base crude oils contain from 10 to 25 per cent of petroleum wax. In the process of dewaxing, this is removed in petrolatum which may contain from 25 to 40 per cent of petroleum wax. The separation of petroleum wax from petrolatum by crystalliza-

tion in a solvent and filtration produces the so-called petroleum ceresin which differs substantially from paraffin wax and somewhat resembles the ceresin obtainable from ozokerite. The content of petroleum wax or ceresin in commercial ceresin may vary from 80 to 95 per cent, depending upon the conditions of crystallization.

Table 123. Content of Petroleum Wax in Various Crude Oils

Origin of Crude Oil	Specific Gravity 60°/60°F	Percentage of Petroleum Wax
<i>United States</i>		
Pennsylvania, average	0.805	2.4
Oklahoma, Tonkawa	0.810	2.1
Oklahoma, Oklahoma City	0.832	4.0
East Texas, Longview	0.831	7.0
West Texas, Pecos	0.881	0.25
Texas, Panhandle	0.810	6.0
Arkansas, Smackover	0.918	2.1
Gulf Coast, Placedo	0.905	0.4
Louisiana, Rodessa	0.810	5.2
California, Santa Fe Springs	0.865	1.5
California, Huntington Beach	0.897	1.9
California, Midway	0.934	0.6
<i>Other Countries</i>		
Mexico, Poza Rica	0.873	3.9
Mexico, Panuco	0.988	0.58
Venezuela, La Concepcion	0.850	3.6
Venezuela, La Rosa	0.910	0.7
Venezuela, Lagunillas	0.950	0.35
Russia, Surachany (Baku)	0.860	2.5; 6.0*
Russia, Balachany (Baku)	0.867	0.8; 2.0*
Russia, Bibi-Eibat (Baku)	0.865	0.4; 1.3*
Russia, Emba-Dossor	0.859	0.3
Russia, Grozny (Waxy)	0.838	6.5; 8.5*
Russia, Grozny	0.875	0.3
Russia, Maikop	0.830	0.5
Roumania, Moreni	0.795	4.8
Roumania, Bustenari	0.835	0.45
Iraq, Kirkuk	0.844	1.9
Iran, Maidan-i-Naftun	0.837	4.5
Burma	0.835	8.0
Assam	0.856	10.7

*The first figure of the wax content has been obtained by the destructive distillation method and the second figure without the distillation (Chapter 3).

The content of petroleum wax in raw rod wax varies from 50 to 70 per cent, the remainder being oils and asphaltic-resinous substances. The melting point of purified rod waxes is from 55 to 82°C (130 to 180°F) (Reistle and Blade)⁴⁷.

Normal Paraffins in Petroleum Waxes

The question of the chemical structure of petroleum waxes is comparatively old. Zaloziecky made a distinction between distilled crystalline paraffin wax consisting of normal paraffin hydrocarbons and the virgin amorphous petroleum wax made up of isoparaffins. The amorphous isoparaffins of crude oils are transformed into crystalline normal paraffins by cracking or splitting of side chains, which takes place on distillation.

Gurwitch¹⁷ was the first to show that there is no essential difference in the crystalline structure of distilled and virgin petroleum waxes. The virgin "amorphous" petroleum wax is in reality crystalline, but the size of the crystals is much less than in the case of distilled paraffin waxes. Sachanen and Bestougeff⁵¹ showed further that virgin petroleum waxes, separated directly from a crude oil, dissolve in oils and organic solvents, forming saturated solutions. Their solubility changes with temperature in the same manner as that of distilled paraffin waxes and other crystalline substances.

On the other hand, Zaloziecky's assumption that distilled paraffin waxes are normal paraffins has been proved to be correct, at least to a great extent. As will be seen later, commercial paraffin waxes are predominantly normal paraffins. Isoparaffins are also present in distilled paraffin waxes, particularly in residues.

The proofs that the commercial paraffin waxes consist mostly of normal paraffins are numerous and convincing. First, Krafft²⁹ showed that the narrow fractions of paraffin wax from a brown coal tar had the same properties as the individual normal paraffins synthesized by this experimenter.²⁸ The data of Francis *et al.*¹⁴ also show that the hydrocarbons of shale paraffin wax correspond more or less to normal paraffins. Mabery³¹ fractionated a commercial paraffin wax and separated paraffins from $C_{23}H_{48}$ to $C_{29}H_{60}$, the melting points of which corresponded to those of normal paraffins.

Carpenter⁷ studied the fractions obtained from Burma petroleum waxes. The melting point of the fractions varied from 41 to 71.7°C. The waxes consisted of a series of paraffins, from $C_{21}H_{44}$ to $C_{34}H_{70}$. Higher molecular weight hydrocarbons were obtained from sucker rod wax from the same crude oil. The properties of the fractions corresponded closely to those of normal paraffins. However, some anomalies in the molecular weight in the case of 66.5°C and 70.0°C waxes suggested the possibility of the presence of isomeric paraffins.

Buchler and Graves⁶ studied the narrow fractions of the waxes produced from paraffin wax, slop wax, petrolatum wax, and rod wax of Salt Creek crude oil (Wyoming). Each wax was recrystallized from ethene chloride at 40°F until one of constant melting point and refractive index was obtained. The oil-free wax was then fractionated under a pressure of less than 1 mm of mercury. Thus, each of the four waxes was resolved into a series of narrow fractions, whose melting points and refractive indices (at 84°C) were determined. When the values of refractive index were plotted against the melting points, it was shown that the refractive indices of the lower fractions fell approximately on a straight line, whereas those of the higher fractions (melting points above 55°C) were markedly higher. The authors believed that this discrepancy was due to the presence of some unknown impurity which was removed by hot crystallization at 35-40°C in ethene dichloride. In this way a very small amount of "waxy impurity" or "soft wax" was obtained. The refractive

index of the fractions purified by this method and plotted versus melting point, gave a straight line. The physical properties of the purified fractions were very close to those of synthetic normal paraffins. The authors concluded that petroleum waxes consist of straight-chain paraffins and an admixture of "soft wax," which affects the crystallization of paraffins, as will be seen later.

It should be pointed out that repeated crystallization and separation of petroleum waxes ("until a wax of constant melting point and refractive index was obtained") and further crystallization in hot solvent will remove completely all isoparaffins which are of lower melting point and higher solubility in solvents. Thus, it is not surprising that the purified petroleum waxes turned out to be normal paraffins. Neither the petroleum waxes removed by crystallization nor the "soft wax" were investigated by the authors who, for this reason, failed to show the presence of branched paraffins in petroleum waxes.

The normal structure of the paraffins composing commercial paraffin waxes should not be understood too literally. The "terminal" isoparaffins with short side chains, *e.g.*, isoparaffins with one methyl group in position 2, do not differ appreciably in their physical properties from normal paraffins of the same molecular weight. The melting point of such isoparaffins in paraffin waxes would be 5 to 10°C lower, and their solubility in various solvents correspondingly greater as compared with normal paraffins of the same number of carbon atoms. The specific gravity and refractive index would be close to those of normal paraffins. Therefore the presence in paraffin wax of such terminal isoparaffins with short side chains cannot be ruled out.

The action of fuming sulfuric acid or chlorosulfonic acid on the isoparaffins in question is unknown. If these reagents react with the terminal isoparaffins in the same manner as with other branched paraffins (see the next section), the reaction may be used for the clarification of this problem, as well as other appropriate methods, including the x-ray and infrared rays methods.

Sachanen and Tilicheyev⁵³ showed that the cracking of commercial paraffin wax yields hydrocarbons of normal structure. A commercial paraffin wax, melting point 57-58°C, was found on fractionation to consist mostly of $C_{24}H_{50}$ to $C_{26}H_{54}$ paraffins. Cracking under moderate temperature-time conditions gave liquid products which were then fractionated, treated with sulfuric acid, and redistilled to remove unsaturated hydrocarbons. The treated fractions were highly paraffinic and contained about 10 per cent of naphthenes. Recrystallization of the fractions produced pure normal paraffins of various molecular weights up to $C_{17}H_{36}$. Thus, normal paraffins are formed as a result of cracking $C_{24}H_{50}$ — $C_{26}H_{56}$ hydrocarbons of commercial paraffin wax.

By this method, normal paraffins of lower molecular weight (up to $C_{20}H_{42}$) can be prepared from commercial paraffin wax. Olefins of various molecular weights, and also of normal structure, are formed by this

method in an amount approximately equal to that of normal paraffins.

The long paraffinic chains of paraffin wax can be used for alkylation of aromatic hydrocarbons and compounds. This process is being used on a commercial scale. Paraffin wax is chlorinated to produce a chlorowax which then reacts with such aromatics as naphthalene or phenol, in the presence of aluminum chloride to effect alkylation. Naphthalene or phenol with long paraffinic side chains are formed (Paraffow and Santapour respectively); these are used as pour-point depressants for lubricating oils.

It can be stated on the basis of the above studies that commercial paraffin waxes are mixtures mostly of normal paraffins from $C_{22}H_{46}$ to $C_{30}H_{62}$, the proportion of which depends upon the melting point of the wax. Normal hydrocarbons of higher molecular weights can be separated from such wax products as petrolatum wax, rod wax, etc. The separation of normal paraffins from these waxes, however, is more difficult in view of the presence of isoparaffins, as will be shown later.

Isoparaffins in Petroleum Waxes

Ferris, Cowles and Henderson¹² investigated narrow fractions of a paraffin wax from a Mid-Continent crude oil. These were separated by fractionation of oil-free waxes at an absolute pressure of less than 1 mm of mercury in a 5-foot column. The fractions obtained had boiling ranges of approximately 15°C. The oil-free waxes were obtained separately from scale wax, slack wax, foots oil and sweat oil by successive crystallization from ethene dichloride at -18°C. The fractions having identical 50 per cent boiling points or refractive indices varied widely in melting point, particularly the high-boiling (or high refractive index) ones. The fractions produced from scale wax had higher melting points than those produced from slack wax, etc.; those from sweat oil had the lowest melting points. By systematic crystallization of two fractions of about the same boiling range, six more uniform fractions having practically the same molecular weight and boiling range were obtained, whereas their other properties, such as melting point, specific gravity, etc., were quite different (Table 124).

Table 124. Data on Paraffin Wax Fractions.

Fraction:	A	B	C	D	E	F
50% boiling point at 10 mm	269.5	269.5	272.0	272.0	272.0	273.0
Molecular weight	366	367	379	389	385	375
Average value of n in C_nH_{2n+2}	26	26	27	27.6	27.4	26.8
Melting point (°C)	59.9	55.2	47.1	40.5	35.2	29.4
Refractive index at 80°C	1.4303	1.4306	1.4330	1.4350	1.4359	1.4380
Specific gravity at 80°C	0.770	0.773	0.779	0.783	0.786	0.792
Solubility in ethene dichloride at 14°C per 100 cc	0.115	0.218	0.82	2.4	5.7	70.3
Molecular refraction observed	122.7	122.8	126.5	129.8	128.4	125.0
Molecular refraction calculated	122.3	122.3	126.9	129.7	128.7	126.0
Yield (%)	59	6	7	9.5	9.5	8

The data obtained cannot be explained on the assumption that waxes of the same boiling range consist of various mixtures of saturated straight-chain hydrocarbons with the "soft" wax. The authors believe that paraffin wax contains not only straight-chain paraffins but also various types of branched paraffins which have lower melting points, higher specific gravities and refractive indices, and greater solubility. The agreement between calculated (on the basis of C_nH_{2n+2}) and observed values of molecular refraction shows that all hydrocarbons are paraffins.

Clark and Smith⁸ studied the x-ray diffraction of fractions A to F (Table 124) investigated by Ferris *et al.* and verified in general the conclusions of these authors. The number of orders of diffraction caused by the oriented molecules decreases from A to F with decreasing melting point. Thus, the degree of perfection of orientation of the molecules decreases with decreasing melting point, indicating that the high melting point fractions consist mostly of oriented, long-chain normal hydrocarbons, whereas the low melting point fractions are more spherical or isoparaffinic.

Yannaquis⁶¹ obtained similar results, having fractionated paraffin waxes by extraction in benzene. The most soluble fractions contained isoparaffins, whereas the least soluble fractions and the residuum consisted predominantly of isoparaffins. Infrared rays were used in this investigation.

Normal paraffins predominate in petroleum waxes from Mid-Continent crudes, particularly in paraffin waxes. According to Sachanen, Wassilieff and Sherdeva,⁵² there are crude oils in which the petroleum waxes are chiefly isoparaffins. These authors studied the narrow fractions of petroleum waxes from two Russian crude oils from the Grozny and Surachany oil fields. The fractions were obtained by crystallization in ethene dichloride and distillation under high vacuum. The molecular weight, specific gravity, melting point and viscosity, as well as the ultimate analysis, were determined for each fraction. The elemental composition and formulas correspond closely to hydrocarbons of the series C_nH_{2n+2} . Fig. 32 represents the melting points of the fractions versus the molecular weight. The same figure also includes the melting points of pure normal paraffins, as well as those of the fractions which were separated by Ferris and marked with x. The curves demonstrate that the melting points of the Grozny petroleum waxes correspond closely to those of normal paraffins, whereas the melting points of Surachany petroleum waxes lie as much as 20°C lower than those of normal paraffins. It is interesting to notice that two paraffin wax fractions of Ferris (Table 124) correspond to normal paraffins, two to isoparaffins found in the Surachany crude, and that two lie between normal and Surachany isoparaffins. The same results are obtained by plotting the specific gravity of petroleum waxes versus molecular weight. Fig. 33 gives the specific gravities of normal paraffins and petroleum waxes separated from Grozny and Surachany crude oils. The data of specific gravity were obtained at 100°C. The

data of Ferris *et al.* determined at 80°C were recalculated to 100°C accepting $\frac{dD}{dt} = -0.00064$. The specific gravities of Grozny petroleum waxes coincide with the curve for normal paraffins, whereas those of Surachany waxes form another curve above the first one for normal paraffins. As with the previous curve for melting points, the two values of specific gravity obtained by Ferris correspond to normal paraffins, two are close to Surachany isoparaffins, and two are intermediate.

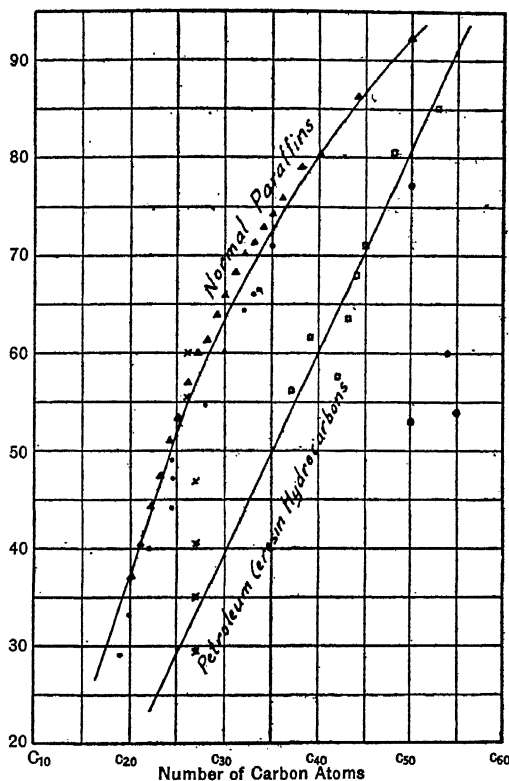


FIGURE 32. Melting points of petroleum wax fractions versus molecular weight.

Kolvoort, Moser and Verver²⁷ fractionated petroleum waxes from Rangoon, Java, and Roumania crude oils. The wax fractions of the Java crude oil correspond to normal paraffins, with the exception of the last fractions. Only the first fractions of the Roumania petroleum wax correspond to normal paraffins. The higher wax fractions of both crude oils have lower melting points and higher specific gravities and are probably isoparaffins. Thus, Borneo, Java and Rangoon crude oils are rich in normal paraffins, whereas Roumania crude oil is richer in isoparaffins.

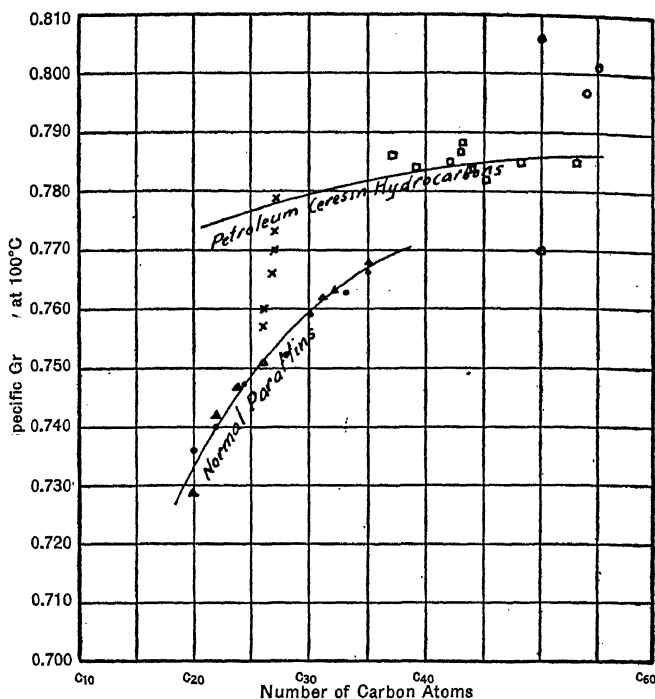


FIGURE 33. Specific gravity of petroleum wax fractions versus molecular weight.

The proportion of isoparaffins in the latter, however, is apparently much lower than in the Surachany crudes.

It should be pointed out that the specific gravity of isoparaffins isolated from the Surachany crude oil, of molecular weight C_{37} to C_{53} , change rather irregularly in the range from 0.782 to 0.787. In any case there is no gradual increase of specific gravity with increasing molecular weight, as it takes place with normal paraffins or wax fractions corresponding to normal paraffins. This peculiarity of Surachany isoparaffins is evidently related to their iso-structure. It is hardly to be expected that the isoparaffins of petroleum waxes would belong to the same homologous series. It seems more probable that the iso-structure of such isoparaffins will vary from fraction to fraction, causing irregularity in the change of specific gravity or refractive index with increasing molecular weight. It should be remembered that the isoparaffins of gasoline fractions also belong to various classes, beginning with slightly branched and ending with highly branched hydrocarbons (compare, for instance, Table 80).

The structure and the degree of branching of isoparaffins from petroleum waxes is unknown. Fig. 32 shows, however, that the melting points of isoparaffins separated from Mid-Continent and Surachany crude oils is on the average 20°C lower than that of normal paraffins. Such a com-

paratively small difference indicates that the degree of branching of the isoparaffins in question is also comparatively small. According to the data systematized by Egloff,¹¹ the difference in the melting point of normal high molecular weight paraffins (C_{18} or more) and those with one or two methyl groups in side chains is from 10 to 30°C. Thus it is probable that the solid isoparaffins of petroleum waxes are slightly branched, for instance, with one or two methyl groups in the side chains. It is interesting to remember that such structures are quite common in low-boiling oil fractions, *e.g.*, in gasolines and naphthas.

Pogacnick⁴⁴ came to the same conclusion on comparing the properties of ceresin fractions and of synthesized isoparaffins. The ceresins are similar to the synthetic isoparaffins with short side chains (methyl and ethyl groups) in the middle of the main chain.

Recent investigations have amplified our knowledge of the branched paraffins and verified the above conclusions. Backer and Strating¹ synthesized some high molecular weight normal and branched paraffins and found that the branching in the middle of the molecule strongly affects the melting point, as the following data clearly show:

Hydrocarbon	Melting Point (°C)
Normal tritetracontane, $C_{43}H_{88}$	85
$CH_3-(CH_2)_{41}-CH_3$	
Methyl-di-heneicosyl-methane, $C_{44}H_{90}$	66.6-61.7
$CH_3-(CH_2)_{20}-\overset{\text{CH}_3}{\underset{ }{CH}}-(CH_2)_{20}-CH_3$	(two modifications)
Nonyl-di-neneicosyl-methane, $C_{52}H_{104}$	32.7-39.0
$CH_3-(CH_2)_{20}-\overset{\text{CH}_3}{\underset{ }{CH}}-(CH_2)_{20}-CH_3$	(two modifications)
C_9H_{19}	

Thus the replacement of a hydrogen atom in the middle of a high molecular weight and high melting point normal paraffin with a methyl group results in the lowering of the melting point approximately 20°C, and with a nonyl group 45°C.

The data of the table by Cosby and Sutherland on page 231 show that the difference in the melting point of *n*-butyldocosanes is as high as 20.8°C by shifting the butyl group from position 5 to position 11. The melting point of normal hexacosane (57°C) drops to 0°C by one butyl branching in the middle of the molecule.

Another proof of the branching of petroleum isoparaffins in the middle or central parts of the molecules is a higher specific gravity (or refractive index) as compared with normal paraffins. Table 125 contains the data on specific gravity and refractive index of normal and isomeric octanes.¹¹

The data show that the specific gravity and refractive index are higher for isomers with side chains in the middle of the molecule, whereas side chains at the ends cause a decrease in the values of these properties as compared with the normal hydrocarbon. Other hydrocarbons give in general the same results as octanes (Boord⁵).

The viscosity of petroleum waxes supposed to be rich in isoparaffins also indicates the iso-structure of these hydrocarbons, as well as the central branching of molecules. Sachanen, Vassilieff and Sherdeva⁵² determined the viscosity of some Grozny and Surachany petroleum wax fractions at 80 and 100°C. The data are included in Fig. 34, in which the viscosities are plotted versus the number of carbon atoms. Curve A corresponds to the viscosity of Grozny paraffin waxes which are, at least chiefly, normal paraffins, as has been proved in the previous sections. Curve B shows the viscosities of the Surachany petroleum ceresins

Table 125. Specific Gravity and Refractive Index of Octanes

Hydrocarbon	Specific Gravity, (D ₄ ²⁰)	Refractive Index (n _D ²⁰)
<i>n</i> -Octane	0.70283	1.3976
2-Methylheptane	0.6978	1.3947
3-Methylheptane	0.7057	1.3983
4-Methylheptane	0.7163	1.3981
3-Ethylhexane	0.7122	1.4020
2,2-Dimethylhexane	0.6956	1.3930
2,3-Dimethylhexane	0.7124	1.4012
2,2,3-Trimethylpentane	0.7162	1.4032
2,2,4-Trimethylpentane	0.6919	1.3916
2,3,3-Trimethylpentane	0.7258	1.4075

which are apparently isoparaffins of a low degree of branching. As will be seen from Fig. 34, Curve B lies much higher than Curve A, indicating that the waxes or isoparaffins of Surachany crude oil are much more viscous than the waxes or normal paraffins of Grozny crude oil at the same molecular weight. The viscosity of isoparaffins branched close to the ends of the molecule is lower than that of normal paraffins of the same molecular weight, whereas the viscosity of isoparaffins branched in the middle, particularly with two side chains, is greater than that of normal hydrocarbons. Thus, the viscosity of petroleum ceresins is another proof of their iso-structure and branching in the central parts of the molecules.

Chemical data on the petroleum waxes are also in accordance with the above conclusions. It is known that isoparaffins are much more susceptible to oxidation reactions than normal paraffins. They react, for instance, with fuming sulfuric or chlorosulfonic acid, whereas normal paraffins are almost inert with respect to these reagents. Accordingly, ceresin from ozokerite reacts with fuming sulfuric or chlorosulfonic acid, whereas paraffin wax is almost inert to these reagents. Holde and Schünemann⁵³ suggested using this difference in the behavior of paraffin waxes and ceresins toward fuming sulfuric acid for the evaluation of the content of paraffin wax in commercial ceresins. Sachanen and Sherdeva found that petroleum waxes separated from Surachany crude oil and consisting of isoparaffins are readily attacked by fuming sulfuric or chlorosulfonic acid. For instance, the treatment of a Surachany ceresin, melting point 84°C, with 800 per cent by weight of fuming sulfuric acid at 100°C decomposed 25.4 per cent of the ceresin, while under the same conditions

a Grozny paraffin wax was practically undecomposed (0.9 per cent loss). With a greater excess of fuming sulfuric acid (35 times with respect to the wax), the decomposition of Surachany waxes was as high as 49.3 to 76.6 per cent.

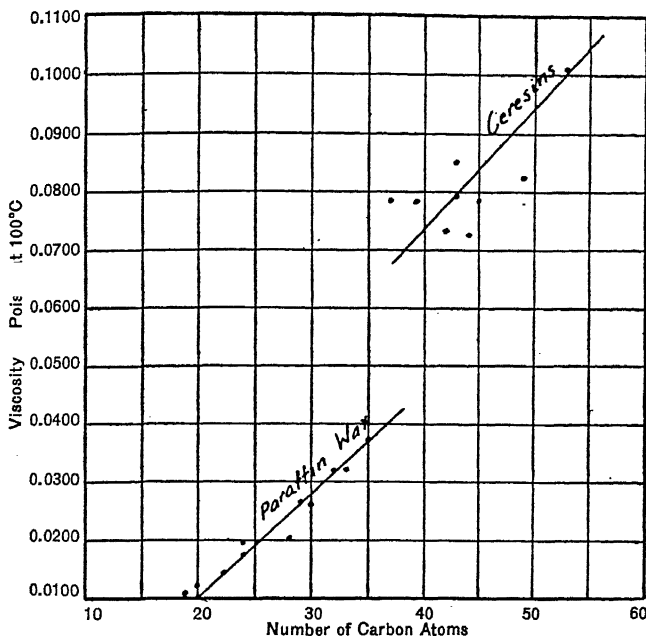


FIGURE 34. Viscosity of petroleum wax fractions versus molecular weight.

An interesting application of the nitration method to commercial paraffin wax and Surachany ceresin has been made by Nametkin and Nifontova.^{39, 40} These authors nitrated commercial paraffin waxes by Konovalov's method and found that the nitro compounds formed were mostly soluble in alcoholic sodium hydroxide, indicating normal hydrocarbon structure. Nitration of a Surachany ceresin (melting point 87.7°C) gave quite different results. A "nitroceresin" insoluble in alkali was formed as a main product (yield 53 per cent), whereas the yield of the impure "nitroparaffins" of normal structure was only 10.7 per cent.

Schaarschmidt⁵⁴ found, however, that commercial paraffin waxes react with antimony pentachloride, and concluded that they contain isoparaffins. This result seems incompatible with the physical properties of these waxes (melting point, specific gravity, refractive index, viscosity), which coincide with those of normal paraffins. This discrepancy may be explained either by the presence of a small proportion of isoparaffins in commercial paraffin wax or by a specific reactivity of high molecular weight normal paraffins with antimony pentachloride.

Zaloziesty's assumption that virgin isoparaffins are transformed into normal paraffins on distillation cannot be accepted in this general form.

Isoparaffins from C_{25} to C_{45} can be distilled with negligible decomposition and without being converted to normal paraffins. Sachanen, Wassilief and Sherdeva⁵² distilled in cathodic vacuum ceresin waxes consisting of isoparaffins C_{35} to C_{45} , without cracking and transformation to normal hydrocarbons. On the other hand, high molecular weight isoparaffins distilled at atmospheric pressure are partially decomposed and give normal paraffins, as proved by Suida and Planckh.⁵⁷ The isoparaffins 16-methylhentriacontane (melting point 34°C) and 16-butyhentriacontane (melting point 23°C) were distilled at atmospheric pressure. The distillates formed were recrystallized from glacial acetic acid and gave a paraffin of melting point $68\text{--}69^{\circ}\text{C}$ in the first case and one of melting point $62\text{--}63^{\circ}\text{C}$ in the second case. Thus the distillation at atmospheric pressure of heavy residues containing isoparaffins of high molecular weight may be accompanied by a partial decomposition of the isoparaffins with formation of normal hydrocarbons.

It may be concluded on the basis of the foregoing discussion that the isoparaffinic structure of the so-called petroleum ceresins has been established firmly. It is understood, however, that commercial petroleum ceresins may contain a variable proportion of normal paraffins. In many cases this proportion may be fairly high due to the fact, to be discussed later, that isoparaffins, even in a moderate proportion, impose their crystalline structure and properties on normal paraffins.

Cyclic Hydrocarbons in Petroleum Waxes

McKittrick, Henriques and Wolff³⁴ made an extensive study of the petroleum waxes separated from distillates, residues, and petrolata of various crude oils. Each petroleum wax was fractionated from ethene dichloride or chloroform. Various fractions were obtained, the last having been produced at -35°C from ethene dichloride and at -55°C from chloroform. The melting points and refractive indices were determined for each fraction. The original paper presents the curves of refractive index versus molecular weight for each wax; these are compared with corresponding curves for hydrocarbons, including normal paraffins, isoparaffins, naphthenes, and aromatics. In one case for Parawax (commercial paraffin wax of the Standard Oil Co. of New Jersey, melting point 51.5°C) the separated fractions (melting points from 37 to 64°C) gave refractive indices which practically correspond to normal paraffins of the same melting point (Fig. 35), the result being in complete accord with the previous conclusions of the preceding sections.

In other cases the curves of refractive index versus melting point are above the curve for normal paraffins and in some cases above that for isoparaffins, indicating the presence of cyclic hydrocarbons. The curves for distillate waxes (Fig. 35) lie nearly parallel and fairly close to the line for normal paraffins in the region of higher melting points. The portion of the curves in the region of lower melting points rises above the normal paraffin line and enters into the region of naphthenes. The au-

thors conclude that the higher-melting fractions of distillate waxes are predominantly normal paraffins, and that the lower-melting fractions, as well as the waxes of residues and petrolata, are rich in naphthenes and aromatics.

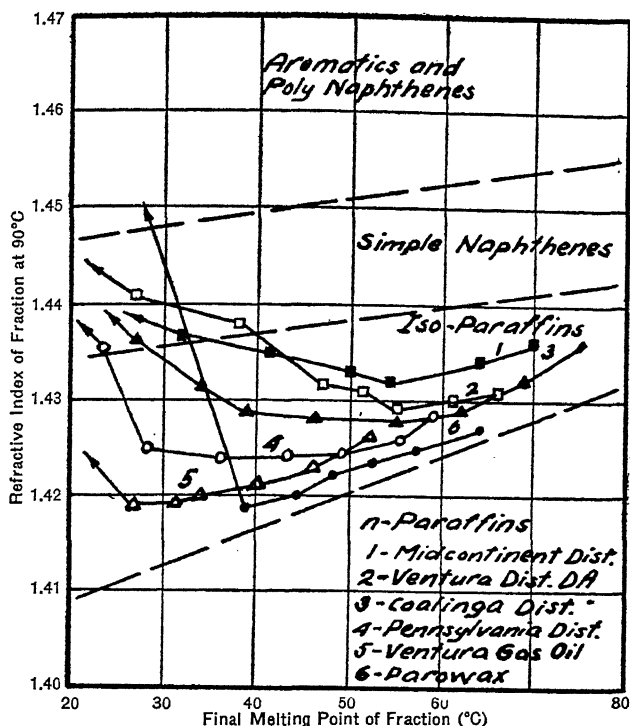


FIGURE 35. Refractive index of petroleum wax fractions from various crude oils (Courtesy *Journal of the Institution of Petroleum Technologists*)

These conclusions, however, do not seem to be convincing. The data on the purity of the fractions produced and the ultimate analyses are lacking. As a matter of fact, the abnormally high values of refractive index of the fractions may be due to the impurities or to the presence of naphthenic and aromatic hydrocarbons. It is significant that the greatest deviations from the lines of paraffins were observed for low-melting waxes (20 to 40°C). These fractions were obtained at very low temperatures of crystallization, from -35 to -55°C, and might be particularly impure. As will be seen from comparison of Table 124 and Fig. 35, there is a considerable difference in refractive indices between the data of Ferris *et al.* and those of McKittrick *et al.* for petroleum wax fractions from Mid-Continent crude oils. The last data are invariably higher than the first, indicating the possible presence of highly refractive naphthenic hydrocarbons. Greater deviations of residue- and petrolatum-wax fractions

from paraffins might be attributed to the greater difficulties of separating pure waxes from viscous oils.

The earlier data of Müller and Pilat³⁸ on the presence of cyclic paraffin waxes appear to be more convincing. They found that petroleum waxes separated from asphalts have a chemical composition corresponding to the formula C_nH_{2n-m} . A sample of asphalt from a Boryslav crude oil was shaken with an excess of petroleum ether. The petroleum wax obtained after evaporation of the ether was crystallized twice from pyridine. Further refining was carried out by decolorization with charcoal in hot benzene and by subsequent crystallization from ether. By fractionation from benzene the wax was separated into four portions with melting points from 49-56° to 75-80.5°C and molecular weights from 695 to 775. The iodine numbers ranged from 1.4 to 4.1. The formulas of the fractions corresponded to $C_nH_{2n+0.8}$ to $C_nH_{2n-3.1}$, indicating cyclic structure. The specific gravities and refractive indices of the fractions were appreciably higher than those of the corresponding paraffins.

Another petroleum wax was separated from a Boryslav crude oil by fractionation with methane at low temperatures and by precipitation of the asphalt-free residuum with alcohol. The wax precipitated was crystallized from pyridine-alcohol, then from acetone-benzene, and finally from ether. The second fraction, more soluble in ether, had the formula $C_{33.2}H_{67.2}$, corresponding to $C_nH_{2n+0.8}$.

The authors believe that the wax fractions produced consisted entirely of waxes due to numerous fractionations. If so, the appreciable deviations from the formula C_nH_{2n+2} are significant and may be considered as a proof of the cyclic structure of these hydrocarbons.

These data for specific gravity and melting point of waxes are plotted in Figs. 32 and 33 and marked with o. The values of specific gravity determined by the authors at 80°C were recalculated for 100°C by using $dD/dt = -0.00064$. It will be clearly seen that the data of Müller and Pilat do not correspond to those of the isoparaffins found in Surachany crude oil. The melting points are appreciably lower and the specific gravities are much higher at the same molecular weight as compared with Surachany isoparaffins. These deviations can be explained either by a higher degree of branching or by the cyclic nature of hydrocarbons. The latter conclusion seems more probable and conforms to the formulas found.

Yannaquis⁶¹ studied a commercial paraffin wax of Pechelbronne and its fractions (melting points from 45.1-56.5° to 64.7-67.9°C) by x-rays and in a microscope in polarized light. He found that the waxes have two crystalline forms, one of which is due to paraffins and the other to cyclic hydrocarbons.

Mair and Schicktzan³² performed a series of combustion analyses of three wax samples, obtained by Ferris and his co-workers, with an accuracy of approximately ± 0.0005 for the ratio of hydrogen to carbon. The samples contained a small proportion of some oxygen compounds. Cor-

rections were calculated on the assumption that the oxygen was present in an aldehyde or ketone form. Whereas the high-melting fraction (melting point 65.5°C and molecular weight 420.5) corresponded to the formula $\text{C}_n\text{H}_{2n+2}$, the two low-melting fractions of about the same boiling range and molecular weight (melting points 38.8 and 34.0°C , respectively) had the formulas $\text{C}_n\text{H}_{2n+0.67}$ and $\text{C}_n\text{H}_{2n+0.51}$, respectively. The authors concluded that these wax fractions were composed of about 70 and 75 per cent of molecules of the series C_nH_{2n} , *i.e.*, of monocyclic structure, or of correspondingly smaller amounts of molecules of polycyclic hydrocarbons. Thus, it is not improbable that the so-called isoparaffins may contain a certain proportion of cyclic hydrocarbons.

Gross and Grodde¹⁵ recently developed a series of empirical relationships between the molecular weight, density, and solidification point of petroleum waxes, on the basis of which the hydrocarbon structure of petroleum wax may be evaluated. The "ring value" of paraffin waxes is calculated by the equation:

$$\text{Ring value} = 10^3 \times d_{40} - 511 - 311 \times \frac{M}{M + 95}$$

and

$$\text{Asymmetry number} = \frac{311M}{M + 95} - 205 - 0.75 \times \text{Solid. point}$$

The ring value and asymmetry number of normal paraffins are zero, of isoparaffins slightly positive, and of cyclic hydrocarbons positive. The calculations by the author of the ring values for narrow fractions of Grozny paraffin waxes (Fig. 33) has given figures fluctuating from $+1$ to -2 , for Surachany ceresins (Fig. 33) from $+4$ to $+12$, and for the two narrow fractions (mp 38.8 and 34°C) investigated by Mair and Schicktan, $+13$ and $+20$. The asymmetry numbers varied for the above products from 0 to 4 , from 4 to 12 , and from 20 to 24 , respectively.

As a result of studies referred to in these sections, a general conclusion should be drawn that the petroleum waxes consist predominantly of paraffin hydrocarbons. Normal paraffins predominate in commercial paraffin waxes because isoparaffins of the same boiling range are more soluble in oils and are separated in the operations of crystallization and sweating. Branched isoparaffins of lower melting point and higher solubility are present in all distilled fractions containing petroleum waxes. In general, the high-boiling fractions and residues contain a larger proportion of branched paraffins. The nature of the crude oils is another factor affecting the proportion of branched paraffins. There are some crudes which are particularly rich in branched solid paraffins, as, for example, Surachany. The petroleum waxes of most paraffin and mixed-base crudes, however, consist chiefly of normal paraffins.

The isoparaffins of petroleum waxes probably belong to comparatively slightly branched isoparaffins with branches in the middle or in

the central parts of their molecules. The presence of cyclic petroleum waxes, *i.e.*, solid waxy hydrocarbons of cyclic structure with long paraffinic side chains, has not been definitely proved, but seems probable.

Ozokerite Ceresins

Isoparaffinic petroleum waxes or petroleum ceresins are similar to ceresins produced from natural ozokerites. Holde²¹ summarizes the properties of natural ceresins (from ozokerite), petroleum ceresins and paraffin waxes in a table which is given in an abbreviated form (Table 126).

The data of Table 126 show that the physical properties of ceresins from ozokerite are similar to those of petroleum ceresins. The high viscosity of natural ceresins should be pointed out. As mentioned above, natural ceresins react with fuming sulfuric acid or with nitric acid in the same manner as petroleum ceresins. Thus, the chemical structure of natural ceresins should be the same as that of petroleum ceresins, *i.e.*, the former should consist of isoparaffins with comparatively short side chains in the central part of their molecules and possibly, to a lesser extent, of cyclic paraffins. As in petroleum waxes, the cyclic hydrocarbons in natural ceresins may be present in only small percentages. The chemical composition of the natural ceresins corresponds in general to paraffins. As early as 1919, Marcusson³³ showed that various chemical reactions of ceresins and the results of cracking reveal nothing to indicate a cyclic structure.

Table 126. Physical Properties of Ceresins and Paraffin Waxes.

Material	Melting Point (°C)	Density at 20°C 100°C		Viscosity at 100°C in (centi-poise) (centi-strokes)		Nitrobenzene Point (°C)	M. W.
Ceresin from ozokerite	56-87	0.909-0.942		5.2-12.7	6.7-16.2		430-755
Ceresin from Russian crudes	56-85	0.922-0.941	0.783 0.788	6.4-10.1	8.2-12.9	75-89	525-741
Ceresin from American crudes	61-78	0.912-0.933		7.6-9.6	9.4-12.1		
Paraffin wax, Asia	53-75	0.906-0.932		2.5-5.4	3.3-7.0		367-399
Paraffin wax, petroleum and brown coal	42-56	0.867-0.920		2.2-2.7	3.2-3.7		326-501
Paraffin wax, Russian crudes	40-71	0.879-0.933	0.740-0.766	1.45-3.7	1.96-4.84	47.6-69.2	310-492
Paraffin wax, brown coal tar	42-72	0.876-0.921		2.0-4.3	2.6-5.6		

Solubility of Petroleum Waxes in Oil Products

In contradistinction to most other hydrocarbons, petroleum waxes are only sparingly soluble in crude oils and their products at low and moderate temperatures. As a result, oil products containing petroleum wax are of heterogeneous structure due to the presence of petroleum wax crystals. Congelation or solidification of petroleum oils also is a result of the crystallization of petroleum waxes.

The solubility of various petroleum waxes in petroleum oils and other hydrocarbons has been studied by Sachanen⁴⁹ and by Sachanen and Bestougeff.⁵¹ Sachanen studied the solubility of commercial paraffin waxes, *i.e.*, waxes separated from crude oils after distillation. Sachanen and Bestougeff studied the solubility of the so-called protowaxes or virgin petroleum waxes, which are separated from crude oils without distillation. The crudes were treated with sulfuric acid for removal of resins and asphaltic materials and then were precipitated by isoamyl alcohol. Various fractions of protowax were obtained by crystallization from a gasoline. The following general conclusions can be drawn on the basis of these studies:

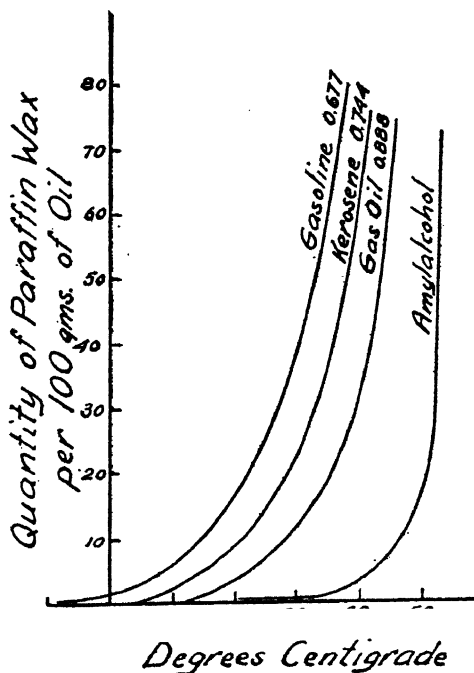
(1) Solubility of a petroleum wax in an oil gradually increases with increasing temperature up to the melting point of the wax, at which temperature the petroleum wax is completely miscible with the oil.

(2) The lower the melting point of a petroleum wax, the higher its solubility in an oil at the same temperature.

(3) The lower the boiling range (or the specific gravity) of an oil fraction the higher the solubility of the same wax in the fraction.

(4) A distilled petroleum wax has the same solubility curve as a virgin (undistilled) wax of the same melting point. Fig. 36 gives an idea

FIGURE 36. Solubility of paraffin wax (melting point 55°).



of the solubility of a paraffin wax in gasoline and other petroleum distillates. Sullivan *et al.*,^{57a} Weber and Dunlap,^{60a} and recently Berne-Allen and Work² also studied the solubility of petroleum waxes in various

petroleum fractions and confirmed the results of the authors cited. The last authors gave a chart for calculation of their solubility values. Bray and Bahlke⁵⁴ have given the data on the solubility of a paraffin wax in low-boiling hydrocarbons: the solubility at the same temperature is maximum for normal hexane and gradually decreases for normal pentane, liquid butane, and propane. The solubility of the paraffin wax in liquid propane is about the same as in normal decane. Thus the above general conclusion (3) has a limitation for low molecular weight paraffins.

These and other investigations have solved the old question of the crystalline or colloidal structure of petroleum waxes, distilled and virgin. Both types, *i.e.*, distilled waxes and protowaxes, are crystalline substances strictly following the conventional laws of solubility. The slope of the solubility curves in gasolines shows that the solution is accompanied by a negative thermal effect amounting to $-52,000$ Cal. by calculation from the solubility curves and to $-48,000$ Cal. by direct determination.⁴⁹ Sullivan *et al.*^{57a} found $-40,300$ Cal. for heavier distillates.

Pour Points of Petroleum Products Containing Waxes

Sachanen⁴⁹ studied the congealing of petroleum oils containing petroleum waxes. This study was performed in light oils in which the crystallization of petroleum wax can be easily observed. There is a very short temperature range between the beginning of crystallization and the congealing temperature, or the pour point (stock point). Fig. 37 repre-

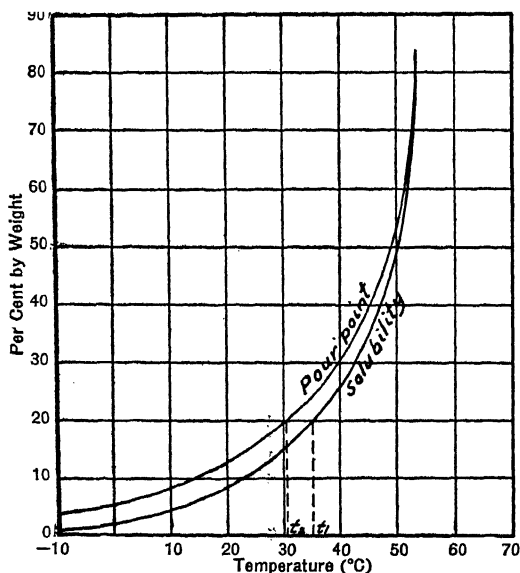


FIGURE 37. Solubility of paraffin wax and pour points of solutions.

sents the solubility and pour-point temperature curves of a petroleum wax in a petroleum fraction. Like the previous curves, the solubility concentrations, as well as the pour-point concentrations, are plotted

versus the temperature. If the crystals of a petroleum wax in an oil begin to form at temperature t_1 and the oil product congeals at temperature t_2 , the difference, $t_1 - t_2$, may be only from 1 to 2-3 degrees in the right part of the curve, which indicates a rapid increase of solubility with temperature; but this difference may be as high as 10°C in the left part of the curve, where the increase of solubility with increasing temperature is slow.

The congealing of oils containing petroleum wax is caused by the formation of a fine and dense crystalline wax structure, which obstructs free movement of the liquid oil. The action of the wax structure is frequently compared with that of a sponge, which may retain in its cells a considerable quantity of water. A comparatively small amount of petroleum wax—about 1 per cent—is sufficient to cause congealing of the oil at 10° to 20° . Thus the structure of the petroleum wax crystals must be very fine and the surface area extremely large. It is not improbable that the purely mechanical effect of the congealing, caused by formation of the wax sponge, is supported by the forces of adsorption of oil on the surface of the wax crystals. This results in an enormous decrease in surface tension and in a corresponding development of the surface of the crystals.

Questions related to the crystalline structure of petroleum wax crystals are to be considered in the next section; the factors affecting the pour point and congealing of petroleum products are discussed below.

(1) The nature of petroleum wax and oil affects the pour point. With the same petroleum product and the same concentration of petroleum wax, the pour point is higher for a high melting-point wax because of its lower solubility compared with a wax of low melting point. With the same petroleum wax in the same concentration, the pour point depends on the boiling range of the petroleum: the higher the boiling range the higher the pour point, because of the lower solubility of petroleum waxes in high-boiling petroleum products. There are no comparative data on the pour points of petroleum products containing an equal percentage of a paraffin wax and a ceresin wax of the same melting point.

(2) The pour point of petroleum products is appreciably lower in the presence of resinous and asphaltic substances. These substances are adsorbed by the surface of petroleum wax crystals and prevent the development of a well formed crystalline structure. As a result, the pour point of a residue containing a petroleum wax and resinous-asphaltic compounds appreciably increases after the resins and asphalts have been removed by chemical treatment. The pour point of steam-refined residues usually increases by 20° - 30°F after filtration through fuller's earth.

(3) The presence of liquid or solid cyclic compounds containing very long paraffinic side chains also affects the pour point of petroleum products containing waxes. The compounds in question, such as paraffin wax naphthalene (Parafflow) or paraffin wax phenols (Santopour), are used to a large extent to depress the pour point of commercial lubricating oils,

particularly of motor oils. Pour-point depressants, even in such small proportions as $\frac{1}{8}$ -1 per cent, may decrease the pour point 40°F or more.^{9, 45, 46} The effect is selective and depends on the nature of the oil to be treated and on the pour-point depressant. The mechanism of the action of pour-point depressants is apparently the same as in the case of resinous and asphaltic compounds, *i.e.*, polar pour-point depressants are adsorbed on the surface of petroleum wax crystals and prevent formation of the sponge structure. It is of interest that pour-point depressants do not change the cloud points of oils and therefore do not affect the solubility of petroleum waxes. Some details on the crystalline structure of petroleum waxes in the presence of pour-point depressants will be discussed later.

(4) Rate of chilling and particularly thermal pretreatment are important factors affecting the congealing of oils. It has been observed by Holde and others that preheating to a certain temperature may decrease or increase the pour point; the residual oils containing petroleum wax are particularly sensitive to this treatment. Preheating to a temperature of about 40-50° usually gives the highest pour points, whereas preheating up to 100° results in the reverse effect. Fig. 38 represents the pour points

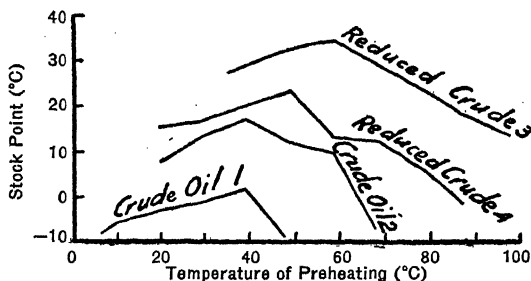


FIGURE 38. Stock points of crude oils and reduced crudes versus temperature of preheating.

of two residues and two crude oils versus the temperature of preheating. It will be seen from these curves that, for instance, for crude oil 1 the maximum pour point, +18°, corresponds to a preheating temperature of 40°, and the minimum pour point, -7°, corresponds to one of +70°. In the same manner Vietti and Oberlin⁶⁰ determined the pour point of a Panhandle crude oil to be +15° without preheating and -17° after thermal treatment at 65°.

The mechanism of this phenomenon (pour point reversion) has been explained by Tytschinin,⁵⁹ who investigated the crystalline structure of residues under a microscope. He showed that residues pretreated at 40-50° produce a network of fine wax crystals, but that the same residues pretreated at higher temperatures form large, loose crystals which do not obstruct the flow of the liquid. Tytschinin's observations were later repeated by Moore and Beard³⁶ on American residues.

The effect of thermal treatment on the crystalline structure of petroleum wax is closely related to the presence of asphaltic and resinous compounds, as has been shown by Tytschinin, Sachanen and Moerbeek and van Beest.³⁵ Removal of resins and asphaltenes by adsorption or by treatment with sulfuric acid decreases the susceptibility of the pour point to thermal pretreatment.

The ascending part of the curve (Fig. 38) may be explained by the gradual dissolution of petroleum wax during preheating, and by the formation of more and more crystallization centers during the cooling period. The asphaltenes are not particularly active in this stage because of their tendency to agglomerate at moderate temperatures. The declining part of the curve may be explained by the activity of asphaltenes at higher temperatures, which bring about their peptization. The crystals formed in this stage adsorb finely peptized asphaltenes on their surfaces and thus prevent formation of the crystalline network. Kreulen³⁰ pointed out the effect of viscosity on thermal pretreatment.

The mechanism of the action of pour-point depressants was investigated by Kolvoort, Moser and Verver.²⁷ The presence of even minute amounts of these, *e.g.*, 0.009-0.04 per cent aluminum stearate, enormously affects the crystallization of petroleum wax, producing large and loosely bound crystals.

Davis and Zimmer¹⁰ studied the effect of pour-point depressants on the crystalline structure of petroleum waxes. The congealing of petroleum oils depends on the net structure as well as on adsorption. The high pour points of oils containing paraffin wax are due partially to mechanical entrainment of oil in the crystalline structure and partially to oil adsorption on the surface of petroleum wax, whereas the high pour points of oils containing petrolatum wax are due almost entirely to oil adsorption. As a result, the oil can be separated from paraffin wax distillate by filtration to a degree determined mostly by the adsorption. On the other hand, the same method fails to separate the oil from petrolatum. Pour-point depressants, because of their polar structure, are easily adsorbed on the surface of petroleum waxes, stopping the growth of wax crystals and thus preventing the formation of a net structure. In addition, the adsorption of a pour-point depressant decreases the adsorption of oil on petrolatum wax crystals and thus diminishes the tendency of petrolata to congeal. Apparently there are no data which would support the idea that pour-point depressants change the solubility of petroleum waxes in oils.

The effect of thermal treatment on the pour point of lubricating oils containing depressants has been recently discussed by Hodges and Boehm,²⁰ Henderson and Annable,¹⁸ and Bondi.⁴ The pour point of pour-depressed oils may be unstable and may also depend upon the thermal pretreatment, as in the case of crude oils and residues. According to Hodges and Boehm, the pour depressant adsorbed by petroleum wax crystals is partially dissolved in the oil upon heating. Upon subsequent

cooling the oil may be adsorbed in preference to the depressant (present in a very small concentration), resulting in increase of the pour point.

It is of interest that modification of the crystalline structure of paraffin waxes can also be effected by the addition of certain high molecular weight polymers. Thomas, Zimmer, Turner, Rosen and Frolich⁵⁸ report that the addition of 1 per cent of polybutenes (molecular weight 15,000) modifies the structure of paraffin waxes.

Crystalline Structure

The crystalline structure of petroleum waxes affects not only the pour point but also other important properties of petroleum products containing waxes, such as the ability of paraffin-wax distillates to be filtered, or of slack waxes to be sweated. Much work has been done to insure the most favorable crystalline structures for pressing and sweating, as well as, in general, to clear up the factors affecting the crystalline structure of petroleum waxes. Summarization of the results of these studies, which are frequently conflicting, presents many difficulties. It is admitted that this question is far from solved.

Theoretically, the following factors may affect the crystalline structure of a petroleum wax in petroleum products:

(1) The nature of the petroleum wax, *i.e.*, its chemical structure (normal paraffin, isoparaffin, etc.) and molecular weight (or melting point for the same series of hydrocarbons).

(2) The nature of the product in which the petroleum wax is crystallized. Various physical and chemical properties of the petroleum may affect the structure of a petroleum wax; viscosity seems to be a factor strongly influencing crystallization and particularly the size of the crystals.

(3) The physical conditions of crystallization, particularly temperature and rate of cooling, as well as thermal pretreatment.

(4) The specific "impurities" which may be present in petroleum products. As has been stated above, the presence of resins, asphaltic compounds and pour-point depressants has a strong effect on the crystalline structure.

The great number of factors affecting the structure of petroleum waxes explains the comparatively slow progress in this phase of petroleum chemistry.

The influence of temperature on the crystalline form of individual paraffins and petroleum waxes in the absence of solvents has been studied during the last ten years. There are at least two crystalline modifications of high-melting normal paraffins. The transition points between two modifications can be determined by cooling or heating curves (temperature versus time) or by other physical methods, including x-rays. Piper and his associates⁴³ found the transition point between two crystalline forms of normal paraffins (from $C_{26}H_{54}$ to $C_{36}H_{74}$) approximately 2 to 6° lower than the melting point. The spread between the melting and

transition points (on heating) equals about 5° for C_{28} to C_{31} , and markedly decreases for high molecular weight paraffins. Müller³⁷ obtained the same results for $C_{24}H_{50}$ to $C_{44}H_{90}$, but the spread between the melting and first transition points was somewhat greater—from 0.5 to 12° .

Kolvoort²⁶ investigated the crystalline structure of individual normal $C_{24}H_{50}$. At room temperature the hydrocarbon has the twin-plate structure, probably monoclinic (γ -form). At a temperature of about 41° it has the first transition point, in equilibrium with the β -form, which is also of the twin structure, but orthorombic. The β -form exists between 41 and 46° , at which temperature it is in equilibrium with the α -form, which crystallizes in needles, probably hexagonal. The α -form exists between 46° and the melting point corresponding to 50.5 - 50.9° . Gray^{15a} extended these results to various high molecular weight paraffins.

Carpenter⁷ was the first to show that commercial paraffin waxes also assume at least two crystalline modifications. The first, or needle form, is stable down to about 10 - 15° below the melting point of a paraffin wax. At this transition temperature the needle form gives way to the plate form ("leafy plates or laminated masses") which is stable at lower temperatures. Carpenter mentioned that another transition point is probable at a still lower temperature. When a paraffin wax is crystallized from a solvent, the form of the crystals also depends upon the temperature: within 15 - 20° of the melting point of the wax, needles are obtained, and below this temperature plates are formed.

According to Katz,²⁵ plates are the basic crystalline form of paraffin waxes, the needle form being a result of transformation of the plate form; in other words, plates would always precede the formation of needles. This finding, however, contradicts the results of Ferris *et al.*,¹³ who showed that needle formation is frequently not preceded by plate formation and that when it is, the plates formed are pseudoplates having little or no resemblance to the typical plates of paraffin wax.

The transition points may be absent in some commercial paraffin waxes, as well as in mixtures of waxes which *per se* have such transition points (Scott-Harley⁵⁵). The differential between the melting and transition points decreases with increasing melting point and with increasing narrowness of the paraffin wax cut.

There is a close similarity in the crystalline form of individual straight-chain paraffins and commercial paraffin waxes.

Seyer, Patterson and Keays⁵⁶ recently investigated the transition points of various normal paraffins from $C_{16}H_{34}$ to $C_{44}H_{90}$. Whereas $C_{16}H_{34}$ and $C_{44}H_{90}$ show no transition points, those from $C_{18}H_{38}$ to $C_{34}H_{70}$ have transition points from 3 - 6° below the melting points. Only one transition point was observed. Nonacosane, the only one odd-numbered member investigated, also gives a transition point. The stable form of this hydrocarbon has a much lower density than of the even-numbered hydrocarbons close to nonacosane.

The rate of cooling and other thermal conditions unquestionably affect the size of petroleum wax crystals, but it is not believed that the crystalline form or modification depend upon these factors. The same is true of the influence of a solvent on crystalline form. For instance, Padgett, Hefley and Henriksen⁴¹ crystallized a commercial paraffin wax from various oils of different viscosity from 60 to 1500 Saybolt seconds at 100°F. The size of the paraffin wax crystals decreased markedly with increasing viscosity, but the shape was apparently similar.

Gurwitch¹⁷ has also shown that the size of petroleum wax crystals decreases with increasing viscosity and asphalt content, but he has over-emphasized the part played by this factor in stating that the different crystalline structure of natural and artificial vaselines is "solely due to the difference of their oily constituents."

On the other hand, Buchler and Graves⁶ apparently exaggerated the effect of "impurities" or "soft wax" on the crystallization of petroleum waxes. According to these authors, pure paraffin hydrocarbons crystallize in plates, whereas oil and the soft wax are responsible for the formation of needles. As has previously been discussed, the formation of needles, or γ -modification, is observed for pure normal paraffins in a suitable range of temperature. The "impurities" do not play any part in the formation of needles by pure paraffin hydrocarbons. The difference between the structure of impure and purified paraffin waxes can be attributed to the presence of another wax modification which is removed in the process of purification.

Ferris, Cowles and Henderson¹³ investigated the crystalline structure of the petroleum wax fractions described in the preceding section. They distinguished three different forms, namely, plate, mal-crystalline, and needle. The mal-crystalline structure is intermediate between plates and needles. The plate type is characteristic of wax fractions which have the maximum melting points at the same molecular weight, *i.e.*, of normal paraffins. The needle crystals are formed by hydrocarbons which have lower melting points for a given molecular weight, *i.e.*, by isoparaffins. Experiments showed that mixtures of needles and plates invariably produced either needles or plates but never mal-formed crystals. Thus, the authors believe that the latter are probably due to another homologous series of isoparaffins than are the needle crystals. The mal-crystalline wax imparts its form upon the plates to a greater extent than does the needle type, when various modifications of petroleum wax are mixed and crystallized. It is important to note that a typical plate wax will invariably crystallize in plates and a pure needle wax in needles, regardless of the solvent or the kind of distillate.

The last statement seems to contradict the results obtained for normal paraffins. It should be kept in mind, however, that the crystallization from solvents took place at room temperature, *i.e.*, much below the transition point of normal paraffins. Thus the plate form of normal paraffins

or paraffin waxes should be expected under these conditions. It is probable that the needle form could be obtained at higher temperatures.

The experimental results of Sachanen, Vassilieff and Sherdeva⁵² are close to those of Ferris and his associates. Sachanen *et al.* found that the ceresins separated from Surachany crude crystallized in needles, in contradistinction to paraffin wax fractions (normal paraffins), which formed plates or their modifications, such as rounded plates, etc. Ceresins impart their needle form to paraffin waxes very easily, so that the admixture of 1 per cent of ceresin to paraffin wax is frequently sufficient to crystallize the latter in needles.

Fig. 39 represents the single-plate crystals of paraffin wax (Katz), Figs. 40 and 41 the plate crystals of paraffin wax (Katz and Sachanen

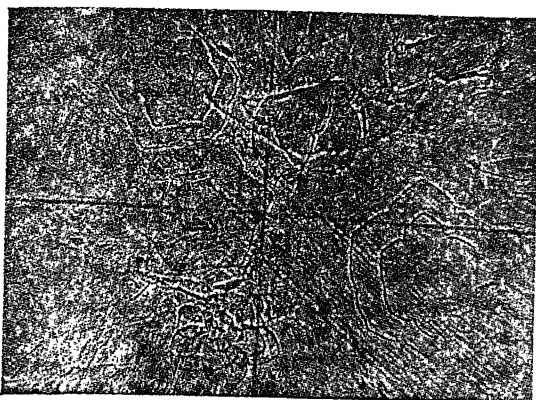


FIGURE 39. Single plate crystals of paraffin wax, X350. (Courtesy *Journal of the Institution of Petroleum Technologists*)



FIGURE 40. Plate crystals of paraffin wax, X350. (Courtesy *Journal of the Institution of Petroleum Technologists*)

et al.), and Figs. 42 and 43 the needle crystals of petroleum ceresins (Sachanen *et al.*).

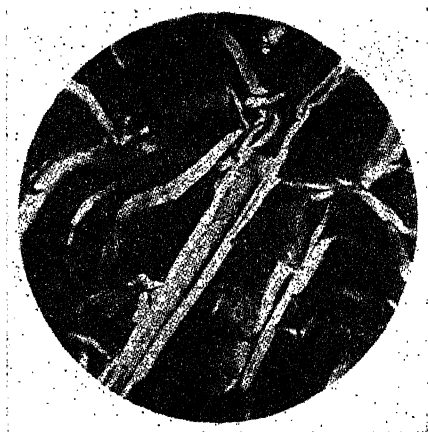


FIGURE 41. Plate crystals of paraffin wax, X170.

The plate is the original crystalline form of paraffin wax at low and moderate temperatures. Rhodes *and al.*⁴⁸ and Ivanovsky²³ pointed out that the various modifications of the plate, such as rounded plates, needles, sticks, funnels etc., are formed as a result of mechanical deformation of the original soft plates, which in the case of low melting point

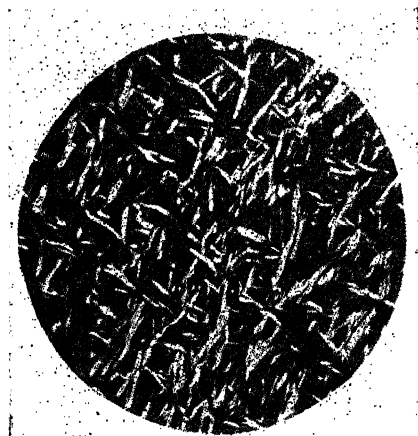


FIGURE 42. Needle crystals of ceresin wax from petroleum, X170.

paraffin waxes, are particularly susceptible to this effect (Katz). The formation of "needles," as a result of deformation of the original plates, may cause a great deal of confusion and explain frequent inconsistencies between the results of various authors.

Conclusions

The following general conclusions may be drawn on the subject of the chemical nature and crystalline structure of petroleum waxes. It is admitted, however, that they cannot be considered as generally accepted and, in many instances, are merely personal views of the author.

Petroleum wax consists of at least two groups of hydrocarbons, which are classified as normal paraffins and isoparaffins. The latter may belong to different homologous series, depending upon the structure and position of the side chains. The side chains of isoparaffins are short and are located in the middle or in the central parts of the molecules. Normal paraffins (and possibly the terminal slightly branched paraffins) crystallize in plates at lower temperatures and in needles at higher temperatures, *i.e.*, from 5 to 10° below the melting point. Isoparaffins are crystallized in needles at any temperature. There is a difference between the needles of normal paraffins and isoparaffins, as will be seen later. If isoparaffins crystallize with normal paraffins, they can impose their needle structure upon them. Cyclic paraffins, the existence of which in petroleum waxes cannot be considered as definitely proved, also may have special crystalline structures.

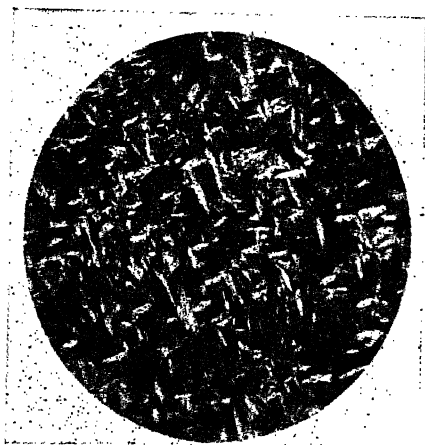


FIGURE 43. Needle crystals of ceresin wax from petroleum, melting point 85°C, X170.

As a rule, normal paraffins and isoparaffins coexist in crude oils. As a result, paraffin distillates contain both. If the boiling range of a paraffin distillate is proper, the distillate will contain normal paraffins of comparatively high melting point and low solubility and isoparaffins of comparatively low melting point and correspondingly high solubility. The crystallization of paraffin wax from such distillates gives predominantly normal paraffins, whereas the isoparaffins remain mostly in solution and are separated in the process of filtration. Thus, paraffin waxes consist chiefly of normal paraffins. The plate form of the crystals insures easy and successful filtration of chilled paraffin distillate. The slack

wax of the plate structure is melted before sweating and may crystallize in needles which insure easy sweating. The formation of needles is due to crystallization above the transition point, as has been discussed above. From this standpoint, it is important to decrease the content of oil in slack wax in the process of filtration as much as possible. Otherwise it will have a melting point much below the transition point, resulting in the plate structure and causing difficulties in sweating.

Too wide a boiling range of a paraffin distillate indicates that it may contain isoparaffins or ceresins of higher melting point and lower solubility. Thus, crystallization will form paraffin wax and ceresin wax simultaneously. The isoparaffins of ceresin wax may impart their fine needle structure and their properties to a paraffin wax and make the filtration process unsatisfactory. According to Peterkin,⁴² the end point of filtrable paraffin distillates from Pennsylvania crudes should be not higher than 285° at 10 mm of mercury, whereas that from a Texas crude oil may be as high as 313°C. Bestougeff³ found the end point of filtrable paraffin distillates from Grozny crude oils to be close to this figure (304°). For such crude oils as Borneo or Rangoon, very rich in normal paraffins and poor in ceresins, the end point of filtrable paraffin distillate may be considerably higher than the figures given above.²⁷

The needles of normal paraffins formed at higher temperatures, and those of isoparaffins and ceresins seem to be entirely different. The former are large and loose, while those of ceresins or paraffin waxes containing ceresins are extremely small and dense. As a result, the needle structure of ceresins prevents sweating entirely. It is well known that the ceresins do not sweat and that they retain the oil very strongly.

Thus, the slack wax produced from a too broad fraction containing comparatively high-melting ceresins may give unsatisfactory results in both filtration and sweating. The proper fractionation of paraffin distillates is of primary importance for both processes. According to Sachanen and his associates,⁵² a very small proportion of ceresin is sufficient to make a normal slack wax unsuitable for sweating. The addition of 5 per cent of ceresin completely changes the plate structure of paraffin waxes, while only 2 per cent of ceresin makes the slack wax resistant to sweating. On the other hand, Ivanovsky²⁴ found that not less than 10 per cent of ceresin is required to change the micro-structure of paraffin waxes.

Other data (Higgs¹⁹) rather confirm the finding of Sachanen *et al.* Higgs stated that the addition of 0.3 per cent of ceresin is "sufficient to render common paraffin wax almost micro-crystalline." If ordinary paraffin wax is dissolved in a solvent and allowed to cool to ordinary temperature, large crystals are gradually deposited, and finally form a porous mass of large, interlacing crystals. If the solution is prepared from paraffin wax and 0.3 per cent of ceresin, a smooth, cream-like mass consisting of very small crystals is obtained on cooling.

The petroleum wax produced from petrolatum or from residual oils

consists of normal paraffins and isoparaffins. The proportion of isoparaffins may vary with the crude oil. In some cases (Surachany) petroleum wax from petrolatum consists predominantly of isoparaffins. In any case, the proportion of isoparaffins in petroleum waxes from petrolata is considerable, and is usually higher than in paraffin distillates. As a result, the fine crystalline structure of isoparaffins or ceresins is imposed upon the petroleum wax obtained from petrolatum. Such petroleum waxes cannot be separated by filtration and refined by sweating.

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Chapter 7

Oxygen Compounds

The oxygen compounds present in petroleum oils either were there originally or are formed in storage or operation as a result of oxidation. The former known as preformed oxygen compounds may be classified as follows: fatty acids, naphthenic acids, phenols, and resinous and asphaltic compounds. The latter of them, which contain sulfur in addition to oxygen and have some properties of high molecular weight colloidal substances, will be discussed in a special chapter. The naphthenic acids differ from fatty acids in their cyclic structure. Fatty and naphthenic acids, as well as phenols, have an acid character and are extracted with alkaline solutions. The term "petroleum acids" adequately covers all the acids extracted from crude petroleum and its products. It is interesting to notice that the preformed oxygen compounds are acids. No other oxygen compounds, such as alcohols, ketones, aldehydes etc., have been detected in crude oils or in cracked products.

The origin of petroleum acids in crude oils and straight-run distillates has long been a matter of discussion. It was suggested by many authors that the petroleum acids, particularly naphthenic acids, are formed by oxidation of certain naphthenic hydrocarbons during refining operations. If this theory is true, the naphthenic acids should be excluded from the class of preformed oxygen compounds. It should be recollected that commercial naphthenic acids in the past were obtained after the treatment of kerosenes with sulfuric acid and, after this, with sodium hydroxide solution, both processes being accompanied by air-blowing. The temperature of these treatments might be as high as 50-60°. Gurwitch³⁰ showed, however, that the naphthenic acids extracted from kerosene after the acid-alkali treatment do not differ from those obtained directly from the kerosene distillate. Von Braun³ compared the naphthenic acids extracted from a raw Roumanian crude oil and from distillates and found that they were identical, with the exception of the low-boiling acids which were not in the crude oil and apparently were formed as a result of decomposition of some high molecular weight acids. Von Pilat and Reyman⁶⁸ obtained similar results with a Polish crude oil and its distillates. Tanaka and Nagai⁸² found that the naphthenic acids extracted from oil distillates after treatment with sulfuric acid and before this treatment are practically identical. In addition, von Braun and Wittmayer⁷ studied the naphthenic acids produced from the solvent extract and raffinate of a California kerosene by treatment with sodium

hydroxide and found no difference. The formation of naphthenic acids by oxidation during the treatment would produce quite different acids from the extract and the raffinate.

On the basis of these studies, naphthenic acids should be considered as preëxisting in crude oils. No formation of naphthenic acids takes place on distillation or oxidation during the refining processes. The question of the origin of low molecular weight fatty acids is less clear and still awaits solution. Such acids can be formed as a result of cracking certain unstable high molecular weight acids on distillation.

Determination and Separation of Petroleum Acids

The total amount of acids present in petroleum oils can be estimated by titration with alcoholic solution of potassium hydroxide (usually 0.1 normal). Phenolphthalein or Alkaliblau 6B or thymolphthalein for dark oils are used as indicators. The neutralization number or the acidity is the weight in milligrams of potassium hydroxide required for neutralization of one gram of the oil. The content of petroleum acids can be calculated from the neutralization number, if the average molecular weight of the acids is known. Such a calculation for narrow fractions will give fairly accurate results.

The titration takes place in the presence of a 2 to 1 benzene-alcohol mixture. Usually from 5 to 10 volumes of the mixture are taken to 1 volume of the oil to be tested. The quantities of oil varies from 1 to 10 grams, depending on the content of petroleum acids. If the oil is too dark, it is extracted with two volumes or more of 96 per cent alcohol. After the separation, the alcohol extract is titrated with 0.1*N* alcohol potassium hydroxide solution in the presence of Alkaliblau 6B. The extraction is repeated at least one time more to be sure that the extraction of petroleum acids is complete. The extracts are titrated separately. The benzene-alcohol mixture, as well as the 96 per cent alcohol for extraction, must be carefully neutralized before use. The titration may also be carried out potentiometrically.

The separation of petroleum acids present in oil products is carried out by aqueous or alcohol-aqueous solutions of sodium or potassium hydroxide. Soaps and phenolates soluble in water or alcohol-water are formed as a result of this treatment. The concentration of sodium hydroxide solution, used for extraction of the acids, is from 3 to 10 per cent. The higher concentrations cause the formation of stable emulsions. A single treatment of oil products with sodium hydroxide solution is frequently insufficient for complete extraction of petroleum acids, particularly phenols. Thus repeated treatments are recommended in some cases. If the oil product is viscous, a dilution of the product with one or two volumes of benzene is recommended.

The soaps formed are *per se* emulsifying agents for hydrocarbons. As a result, the caustic extracts of petroleum acids are more or less contaminated with hydrocarbons or oil dispersed in the extract. The con-

tent of emulsified oil may vary from a small percentage to 100 per cent or more with respect to the acids extracted. Other conditions being equal, the percentage of emulsified oil increases with increasing boiling range of the fractions. The caustic extracts of crude oils, particularly heavy ones, and residues usually contain a great proportion of oil and resinous-asphaltic materials, which cannot be separated quantitatively from high molecular weight acids. Thus petroleum acids are usually separated from distillates, particularly kerosenes and gas oils containing petroleum acids of moderately high molecular weights.

The caustic extract of petroleum acids is treated with a small excess of an acid, such as hydrochloric or sulfuric. The petroleum acids liberated form an upper layer which is separated from the aqueous solution. The acids produced are mistakenly called "commercial naphthenic acids" and may consist of naphthenic acids proper, phenols and fatty acids in variable proportions. If the acids are extracted from a crude oil or residuum, asphaltogenic acids may also be present. As has been pointed out above, the term "petroleum acids" is more appropriate for the acids extracted *in toto* from oil products. As in most cases naphthenic acids predominate in petroleum or commercial naphthenic acids, this term may be justified for such products.

Raw petroleum acids contain a rather large proportion of oils, from several per cent to 50 per cent or more, depending on the properties of petroleum acids and oils. Separation of the oil from petroleum acids is frequently a very difficult problem. If the acids were extracted from kerosenes or light gas oils, this can be done by steaming the soaps. In the presence of an excess of superheated steam, the volatile kerosene or gas oil, emulsified in the soap, is distilled from the non-volatile soap. Thus treatment of the soap with a strong acid and liberation of the petroleum acids takes place after the removal of emulsified oil and gives petroleum acids which are free of oil to a great extent. The stripping of emulsified oil by steam is used commercially for purification of petroleum acids. Separation of high molecular weight soaps from high-boiling oils by this method is not feasible because of the low volatility of these oils on steaming.

It should be pointed out, however, that even for low molecular weight petroleum acids the separation of oils by steaming is not quantitative; a small proportion of oils remains in the soap so treated.

Another method is extraction of the oil from soaps with a solvent, for instance, ether or benzene. An equal volume of alcohol is added to the soap solution to prevent the formation of stable emulsions. The soap solution must not contain any considerable excess of free sodium hydroxide. Treatment with the solvent is repeated several times to insure complete removal of the oils. This method gives fairly good results for naphthenic soaps of moderately high molecular weight but seems to be quite unsatisfactory for high molecular weight soaps which tenaciously retain heavy oils emulsified in the soap solution.

Harkness and Bruun³³ and Coheen²⁹ used liquid butane as a solvent for removing oils from naphthenic acids. The raw acids were neutralized with alcoholic solution of potassium hydroxide with a slight excess of the reagent (about 10 per cent). The oils were then extracted with liquid butane at 70-90° in a pressure extractor. The soap free of oils was transformed into free acids by the reaction with dilute sulfuric acid. Treatment of petroleum acids with a mixture of petroleum ether and glacial acetic acid also gives a fair separation of hydrocarbons, soluble in ether, from petroleum acids which are dissolved in the acetic acid.

Complete separation of hydrocarbons from naphthenic acids, however, frequently cannot be obtained by the methods described. Von Braun³ recommends converting naphthenic acids into amines which in acid solution do not absorb hydrocarbons; the latter are therefore easily separated, for instance, by extraction with petroleum ether, etc.

Separation of Phenols and Fatty Acids

As stated in the previous section, petroleum acids may contain phenols and fatty acids in addition to naphthenic acids. Separation of phenols from other acids can be accomplished, according to Holzmann and von Pilat,⁴³ as follows. Raw petroleum acids are distilled with superheated steam at temperatures not exceeding 210°. The distillate is treated with a weak (6 per cent) soda solution which converts acids into soaps but does not attack phenols. It is known that phenols are weaker acids than carbon dioxide and thus are not dissolved in soda solutions. The free and unreacted phenols, together with hydrocarbons, are extracted with ether. The phenols are separated from the hydrocarbons by the action of a strong sodium hydroxide solution and by repeated extraction of hydrocarbons, insoluble in the alkaline solution, with ether. High molecular weight phenols which are not distilled in steam distillation remain in the residuum with non-volatile acids and can also be separated by the method described; but the degree of separation is not as good as in the case of distilled phenols.

Klotz and Littman⁴⁷ recommend exact neutralization of the petroleum acids to phenolphthalein with 0.5 N sodium hydroxide. Under these conditions, the phenols are not neutralized and are removed with hydrocarbons by extracting with petroleum ether or ether, as described above. The phenols are then separated from the solvent, dissolved in alkali, purified, recovered from the aqueous solution by acidification, weighed, and titrated repeatedly. Another method of separating phenols is esterification of the acids into methyl esters, as will be described later. The non-esterified phenols are extracted with sodium hydroxide solution.

There are no satisfactory methods for the separation of fatty acids from naphthenic acids. This separation can be performed only for narrow fractions which are obtained by fractionation of crude petroleum acids. Naphthenic acids form salts of bivalent metals which are more soluble in water and alcohols than those of fatty acids boiling in the same

temperature range. Tschitschibabin and his associates^{85, 86} found, for instance, that the solubility of cadmium salts of fatty acids is much lower than of cyclopentylcarbonic acid. Holzmänn and von Pilat⁴³ separated fatty acids in the form of magnesium salts.

Separation of Naphthenic Acids

The qualitative reaction for the naphthenic acids is the so-called Charitschkoff reaction, in which gasoline is colored green when shaken with a solution of sodium naphthenate precipitated by copper sulfate. The copper naphthenate formed is dissolved in gasoline, causing a green color. This method can be used for identification of naphthenic acids from other petroleum acids, as has been suggested by Charitschkoff.^{12, 13} The quantitative separation of naphthenic acids by this method seems questionable.

The solubility of naphthenates of heavy metals in petroleum and other oils is of practical importance, permitting the wide commercial use of such naphthenates as accelerators in drying oils and for other purposes.

The separation of individual naphthenic acids may be carried out by fractionation of purified commercial acids in high vacuum. Harkness and Bruun³³ distilled naphthenic acids in a molecular still to prevent any decomposition. It is preferable, however, to convert the naphthenic acids into methyl esters and to fractionate the methyl esters obtained; these have a lower boiling point and are more stable than the original naphthenic acids. The formation of methyl esters takes place very easily in the presence of anhydrous hydrochloric acid or sulfuric acid. Methyl alcohol containing 2 to 3 per cent of dry hydrogen chloride is used for esterification. Four moles of the alcohol are reacted with one mole of acids with reflux for several hours. If sulfuric acid is used instead of hydrochloric, one mole of the acid per mole of naphthenic acids is added gradually to the mixture of methyl alcohol and naphthenic acids.

Some investigators have recommended esterifying the non-volatile acids at 115-120° by passing alcohol in the vaporous form through the esterification mixture. Under these conditions, the water formed as a result of esterification is removed almost completely. The esters of naphthenic acids formed are separated as an upper layer. Separation is complete after the addition of 4 volumes of water after the esterification has taken place. The esters are washed with soda solution and water, and dried.

The methyl esters are separated by thorough fractionation, and the narrow fractions or individual esters obtained are saponified with alcoholic sodium hydroxide. The unsaponified constituents are extracted and removed with petroleum ether; the soap solution is acidified to liberate free acids, which are separated, washed, dried, and distilled in vacuo.

If the further purification of a naphthenic acid is desirable, the acid may be converted to acyl chloride by reaction with thionyl chloride or phosphorus chloride. The chlorides are converted to the amides by reac-

tion with concentrated ammonia. The amides are solid crystalline substances which can be recrystallized from water, alcohol, and other solvents. Quebedeaux *et al.*⁷³ fractionated the methyl esters of petroleum acids into very narrow fractions, some of which corresponded to individual esters.

Table 127. Content of Petroleum Acids in Various Crude Oils.

Crude Oil	Specific gravity 0°/60°F	Petroleum acids by wt (%)
Pennsylvania, average	0.805	0.03
Oklahoma, Oklahoma City	0.832	0.1
East Texas	0.835	0.03
West Texas	0.880	0.4
Coastal	0.900	0.6
California	0.865	0.3
California	0.930	1.5
Russia, Surachany	0.860	0.3
Russia, Balachany light	0.867	1.0
Russia, Balachany heavy	0.920	1.6
Russia, Bibi-Eibat	0.865	0.7
Russia, Binagady	0.920	1.6
Russia, Grozny	0.838	0.2
Russia, Grozny	0.875	0.7
Roumania, waxy	0.840	0.2
Roumania, asphaltic	0.880	1.6

Content of Petroleum Acids in Crude Oils and Distillates

The approximate content of petroleum acids in crude oils and distillates can be evaluated on the basis of the acidity determined by the method described in the preceding section. Table 127 gives the systematized data on the acidity and the content of petroleum acids in crude oils, and Table 128 the data on the petroleum acids in various distillates of the same crude oil. As discussed above, the petroleum acids determined by titration include fatty and naphthenic acids and phenols. In most cases, however, particularly for petroleum acids extracted from kerosenes and gas oils, naphthenic acids predominate over other acidic constituents, so that the term "commercial naphthenic acids" seems adequate in such cases.

Table 128. Content of Petroleum (Naphthenic) Acids in Various Fractions².

	—Percentage by Weight—	
	Heavy Balachany	Light Balachany
Kerosene	0.69	0.83
Light gas oil	1.60	1.54
Heavy gas oil	2.48	1.65
Spindle oil distillate	2.98	1.57
Engine oil distillate	2.68	1.16
Cylinder oil distillate	1.90	0.82

The percentage of petroleum acids in crude oils varies in a broad range, being maximum in some naphthenic crudes and minimum in paraffin-base and mixed-base types. The asphaltic and heavy crude oils are not particularly rich in petroleum acids. A very high content of petro-

leum acids in some Russian and Roumanian crude is exceptional. Of American crude oils, those of California are comparatively rich in petroleum acids.

The percentage of petroleum acids in different fractions of the same crude increases from light fractions to heavier ones, but in many cases it reaches a maximum in a certain gas oil or lubricating-oil fraction and then decreases (Table 128). Kerosene and gas-oil fractions of some crudes may contain as much as 1 to 2 per cent of petroleum acids. As mentioned above, the petroleum acids in this boiling range belong mostly to the naphthenic acids, which are widely used in various branches of industry. Tanaka and Nagai⁵² give the content of naphthenic acids in a California kerosene distillate (from Long Beach and Santa Fé crudes) as 0.19 per cent. The extraction of naphthenic acids from kerosene or gas oils is commercially feasible, if the percentage of acids equals or exceeds 0.05-0.1 per cent.

Klotz and Littman⁴⁷ give the following data on the content of pure naphthenic acids in commercial products (commercial naphthenic acids):

Origin	Acid No.	Acid No. of Pure Acid	Percentage of— Acid Oil	
Aruba	205	238	86.5	13.5
Roumania	280	295	94.7	5.3
California 160	157	212	74.5	25.5
California 250	255	280	91.1	8.9
Mexico	285	302	94.1	5.9
Austin	248	277	89.3	10.7
B.R.R.	227	246	92.1	7.9

The data on the commercial naphthenic acids from California crude oils, given by Shipp,⁷⁶ are as follows:

Distillate	Spec. Grav.	Acid No.	% of Oils
Naphtha	0.96-0.98	285-315	1-2
Kerosene	0.97-0.99	235-265	2-5
Gas oil	0.98-0.99	165-195	4-18

The average acid number of commercial naphthenic acids, about 250, corresponds to a molecular weight of 224.

The distribution of fatty acids, naphthenic acids and phenols in petroleum acids depends upon the origin of crude oils and distillates. Straight-run distillates are usually relatively rich in naphthenic and fatty acids and poor in phenols. Naphthenic acids are absent in gasolines, because of their high boiling range. The fatty acids and phenols may be present in straight-run gasolines in a very small proportion. On the other hand, naphthenic acids predominate in higher-boiling fractions, including kerosenes and gas oils. For instance, according to Lapkin,⁵¹ the petroleum acids from a Russian gas oil (Grozny crude oil) contain only 3.6 per cent fatty acids. The content of phenols in petroleum acids is also usually small. Klotz and Littman found that phenols in Aruba commercial acids (from Colombian gas oil) are distributed mainly in the low-

and high-boiling ends of the acid, whereas the intermediate fractions are poor in phenols. However, even in the first fraction of the acid, which is richest in phenols, the relative amount of phenols is only about 2 per cent. In some cases the phenols make up an appreciable part of commercial petroleum acids, as has been found by Holzmann and von Pilat⁴³ for a Boryslav kerosene, of which the phenols comprise 45 per cent with reference to the total amount of acids.

Cracked distillates, particularly from naphthenic and asphaltic crude oils, may contain an appreciable percentage of phenols, in some cases as high as 0.1 per cent. It is of practical interest that some cracked gasolines, for instance from California crude oils, are relatively stable with respect to gum formation because of the presence of phenols. Thus, the phenols formed in cracking play the part of natural inhibitors in such cracked products. The treatment of the latter with caustic partially removes the natural inhibitors and makes the gasolines less stable. For instance, the induction period of a raw cracked California gasoline $6\frac{1}{2}$ hours dropped to $2\frac{3}{4}$ hours after caustic treatment. Newton⁶⁴ repeatedly treated a Trinidad cracked gasoline with a 10 per cent solution of sodium hydroxide. Determinations of the induction period gave the following results:

Soda Washes	Induction Period (minutes)
0	1,320
2	495
4	195
6	210
8	195
10	150
12	120

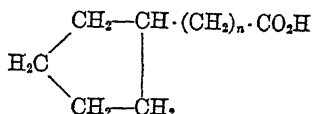
These data show that the phenol present in cracked gasoline may have a great effect on the stability. It should be mentioned also that the complete removal of phenols is comparatively difficult and requires many operations.

The fatty acids may be present in cracked distillates in very small amount; but naphthenic acids are usually absent apparently because of decomposition under cracking conditions.

Individual Naphthenic Acids

Methods of Identification.—The interest paid to the separation and chemical structure of petroleum acids seems surprising, in view of the small proportion of these acids in crude oils. The amount of work devoted to the petroleum acids is as great (if not greater) than that spent on hydrocarbons. Markownikoff and Aschan started the long series of investigations on the petroleum acids more than 50 years ago. Since that time, numerous authors contributed much to this problem. The most work and interest was devoted to the naphthenic acids.

At the present time it is proved that naphthenic acids are the carboxylic acids of the cyclopentane derivatives in which the carboxyl group links mostly to a paraffinic side chain, as for instance:

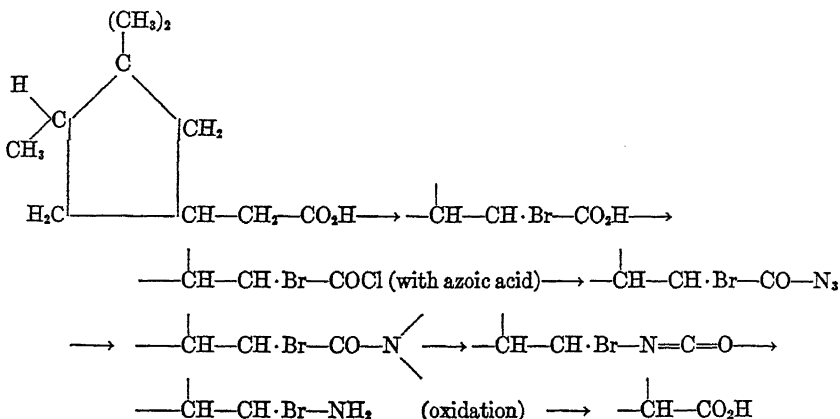


The cyclopentane ring of the naphthenic acids may be more or less alkylated. The acids with $n=1$ predominate. The naphthenic acids with a direct linking of the carboxylic group to the ring ($n=0$) occur much less frequently. The high molecular weight naphthenic acids may also belong to the derivatives of a double naphthenic ring.

The structure of the naphthenic acids was elucidated only a few years ago. Zelinsky⁸⁰ converted naphthenic acids into corresponding hydrocarbons via: acid→ester→alcohol→iodide→hydrocarbon. The reduction of esters into alcohols (the Bouveault-Blanc method) is carried out by the reaction between an ester and metallic sodium in absolute alcohol. The alcohol produced is converted into iodide in the presence of red phosphorus. The iodide is reduced to the hydrocarbon with zinc dust in aqueous alcohol solution. The hydrocarbons produced from naphthenic acids by the methods described could not be dehydrogenated into benzene derivatives by selective catalytic dehydrogenation and had other properties of cyclopentane derivatives.

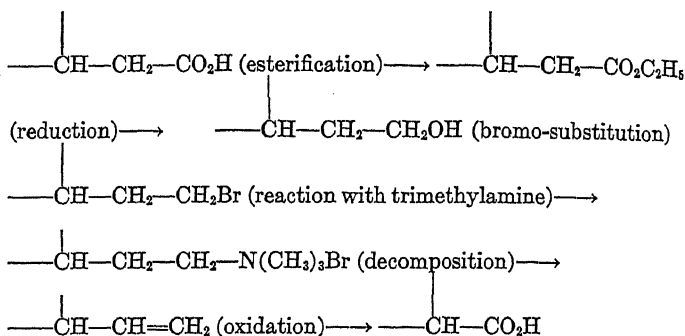
If Zelinsky proved finally that the naphthenic acids are of the five-carbon atom ring structure, von Braun^{3, 4} elucidated the structure of the side chain with the carboxyl group. The methods used by von Braun are those of degradation of the side chain and of conversion of the naphthenic acids to the acids or ketones, in which the carboxyl or carbonyl group is attached directly to the ring.

The first method is illustrated by the following consecutive reactions for one of the naphthenic acids studied by von Braun:



The last acid of known structure was prepared synthetically.

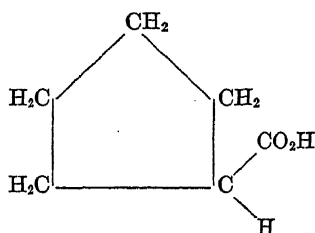
The following reactions illustrate the application of the second method:



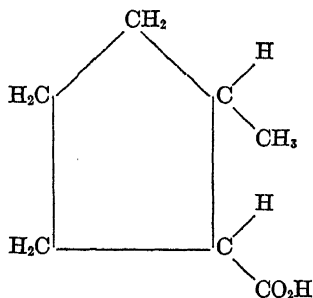
The structure of the last acid is known.

Naphthenic Acids Separated from Petroleum.—Many naphthenic acids have been separated from petroleum acids by fractionation and other appropriate methods in a more or less pure form, but only few of them have been identified. All identified naphthenic acids, with few exceptions, belong to the derivatives of cyclopentane.

The simplest cyclopentane carboxylic or cyclopentylcarboxylic acid



is probably present in Baku petroleum acids, as has been shown by Tschischibabin and his associates.^{85, 86} Nenitzescu, Isacescu and Volrap⁶⁸ identified this acid in petroleum acids from a Roumanian naphtha. The fractions of these acids boiling from 55 to 64° at 20 mm were rich in cyclopentylcarboxylic acid. Ney, *et al.*⁶⁵ detected this acid in a California gasoline and kerosene. 2- or 3-methylcyclopentylcarboxylic acid was iden-

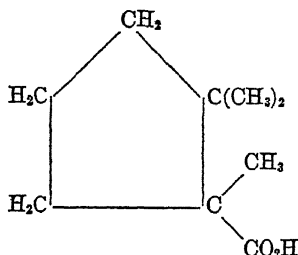


tified by Markovnikoff⁵⁷ and by Aschan¹. Markovnikoff fractionated the methyl esters of Baku petroleum acids and the acids obtained from the esters. The fraction boiling between 215 and 216° (746 mm), $d_{18.5}^{18.5} = 0.9567$, was transformed into amide and amine and identified as methylcyclopentylcarmonic acid. The position of the methyl group, however, has not been determined with certainty. Nenitzescu and Ionescu⁶² found that this acid corresponds to 2-methylcyclopentylcarmonic acid which, however, has the specific gravity 1.021 (20°). Markovnikoff's acid was contaminated with aliphatic fatty acids.

Recently Wash *et al.*⁵⁷ identified 2-methylcyclopentylcarmonic acid in petroleum acids from California crude oils, as well as 3-methylcyclopentylcarmonic acid. The specific gravity of the first acid was 1.0184 (20°), *i.e.*, the same as that of the acid separated by Nenitzescu *et al.*

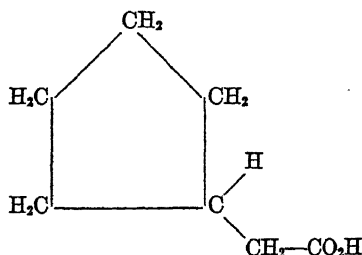
2,2-Dimethylcyclopentylcarmonic acid in a small amount was identified by von Braun³ in the $C_9H_{16}O_2$ fraction of Roumanian petroleum acids by oxidation to trimethylcyclopentanone. The presence of a methylcyclopentylcarmonic acid in this fraction also is probable.

A trimethylcyclopentylcarmonic acid has been separated from Iranian petroleum by Kennedy.⁴⁶ Hancock and Lochte³² isolated solid 1,2,2-trimethylcyclopentyl- or 1,2,5-trimethylcyclopentylcarmonic acid from Signal Hill straight-run gasoline:

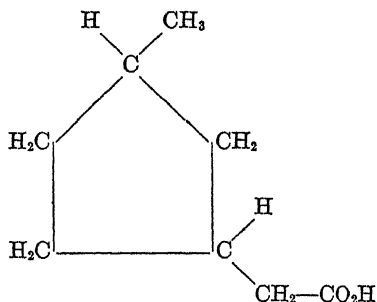


The naphthenic acids of this type, with the carboxylic group attached directly to the cyclopentane ring, are present in crude oils in a comparatively small proportion. Those having the carboxyl group in a paraffinic side chain are more frequent, as has been shown by von Braun.

Nenitzescu, Isacescu and Volrap⁶⁹ and Ney *et al.*⁶⁵ isolated the simplest naphthenic acid of this type—cyclopentylacetic:

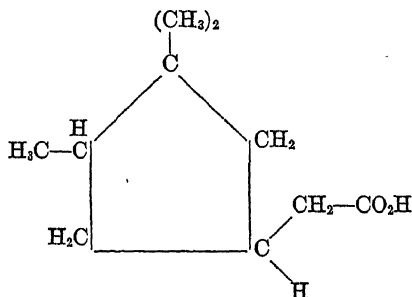


in the fraction of petroleum acids extracted from Roumanian and California naphthas. The next homolog, 3-methylcyclopentylacetic acid



was isolated from the fraction 82-87° of the same petroleum acids. The same acid was isolated from California petroleum acids by Wash *et al.*,⁸⁷ as well as 2,3-dimethylcyclopentylacetic acid.

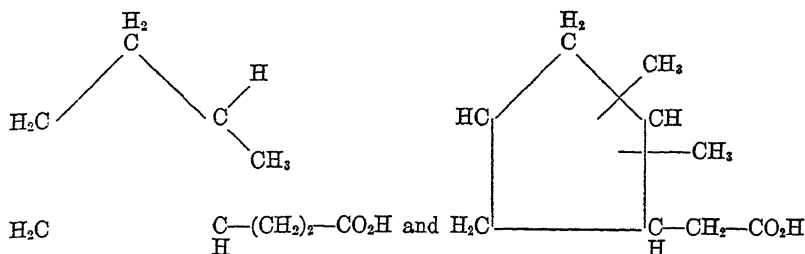
Von Braun identified naphthenic acids of a more complicated structure in petroleum acids. He found³ that the fractions of Roumanian and California petroleum acids corresponding to the empiric formula $C_{10}H_{18}O_2$ have the following structure, *i.e.*, they represent 3,3,4-trimethylcyclopentylacetic acid:



The naphthenic acid of the above structure was synthesized by von Braun, Mannes and Reuter⁶ from 3,3,4-trimethylcyclopentanone. The product is a "completely homogeneous naphthenic acid" because of the absence of numerous isomers which are usually present in naphthenic acids from crude oils or oil products.

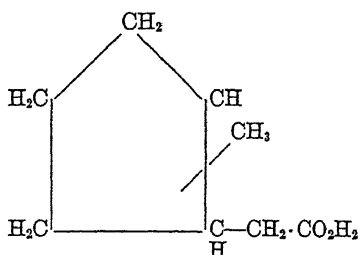
Buchman and Sargent⁹ synthesized 3,3,4-trimethylcyclopentanone by a series of rather involved reactions and found that the ketone synthesized was not identical with that obtained by von Braun from naphthenic acids. Thus they questioned von Braun's structure of certain naphthenic acids related to 3,3,4-trimethylcyclopentanone.

In addition to the above trimethylcyclopentylacetic acid, the fraction of Roumanian naphthenic acids corresponding to $C_9H_{16}O_2$ contains two other naphthenic acids: 2-methylcyclopentylpropionic and dimethylcyclopentylacetic, of the following structural formulas:



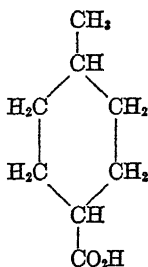
The position of methyl groups, however, is uncertain (von Braun).

The fraction of Roumanian petroleum acids which corresponds to the formula $\text{C}_8\text{H}_{14}\text{O}_2$ contains two isomeric naphthenic acids having the probable structure:



which are isomeric with the above methylcyclopentylacetic acid.

Whereas most of the naphthenic acids, at least of medium molecular weight, belong to the cyclopentane type, some naphthenic acids of the cyclohexane type also occur in small quantities. Kuwata⁵⁰ found a small amount of these in a Japanese crude oil. Tschitschibabin *et al.*^{55, 56} also detected cyclohexylcarmonic acid in the naphthenic acids from Baku crude oils. Cyclohexylcarmonic acid was separated from hexylic acid by crystallization of cadmium salts. Ney *et al.*⁶⁵ separated the same acid from California petroleum. Schulze, Shive and Lochte⁷⁴ isolated from alkali wash from a Texas burner oil (straight-run and cracked) 1,4-methylcyclohexylcarmonic acid (parahexahydrotoluic acid):



This acid was detected in the fractions boiling below 240-241.5°. The melting point of the acid was 108-109°. *Trans*-2,2,6-trimethylcyclohexylcarmonic acid has been synthesized and isolated from Signal Hill straight-

run gasoline by Shive *et al.*⁷⁷ and *cis*-2,2,6-trimethylcyclohexylcarbonic acid was isolated by Ney *et al.*⁶⁵

Naphthenic acids of the formulas $C_{11}H_{20}O_2$ and $C_{12}H_{22}O_2$ separated from various petroleum apparently have a structure more or less similar to that of the acid $C_{10}H_{18}O_2$; but the higher homologs of naphthenic acids have the general formula $C_nH_{2n-4}O_2$ and possess two rings in the molecule, according to von Braun. No more than two rings exist in a molecule of polycyclic naphthenic acids from Roumanian crude oils. Von Braun⁵ synthesized a series of bicyclic naphthenic acids of various structures and compared the specific gravity of these acids with that of the naphthenic acid $C_{13}H_{22}O_2$ produced from a Roumanian petroleum. The specific gravity of the latter was close to that of the acid with two non-condensed cyclopentane rings.

Müller and Pilat⁶¹ studied the high molecular weight naphthenic acids extracted from a Polish lubricating distillate, the formulas of which correspond to $C_{20.4}H_{36}O_2$ to $C_{26.8}H_{45.3}O_{2.3}$. The acids were converted into hydrocarbons by the procedure used by Zelinsky. The regenerated hydrocarbons had a certain proportion of aromatics. The authors believe that the high molecular weight naphthenic acids may also contain aromatic rings.

Harkness and Bruun³³ studied the high molecular weight naphthenic acids from a Gulf Coast petroleum. The reduced Gulf Coast crude oil was distilled over sodium hydroxide to obtain the lubricating distillates. Naphthenic acids in the form of sodium naphthenates were separated and then liberated by reaction with an acid. The acid number of the acids was 166.0; they were distilled in a molecular still under very low pressures. The narrow fractions obtained corresponded to average empiric formulas from $C_{14}H_{23}O_2$ to $C_{29}H_{49}O_2$ and to the type formulas from C_nH_{2n-4} to $C_nH_{2n-10}O_2$. The bromine numbers of the acids were small, from 0.6 to 3.0. The acids were monobasic; and the formulas show that they may contain from one to five naphthenic rings, unless aromatic acids are present in these fractions.

Goheen²⁹ investigated in detail a purified fraction of the naphthenic acids isolated from a Gulf Coast petroleum. This fraction had an average molecular weight of 317, an average molecular formula $C_{20.7}H_{35.2}O_{2.1}$ corresponding to the type formula $C_nH_{2n-6.2}O_{2.1}$. The fraction was converted into ethyl esters which were reduced to alcohols by means of sodium in anhydrous ethyl alcohol; the alcohols were transformed into iodides which were finally reduced to the hydrocarbons by zinc. The raw hydrocarbons had a specific dispersion of 107, denoting a very small proportion of aromatics. Treatment of the hydrocarbons with sulfuric acid confirmed this conclusion. Hydrogenation of the hydrocarbons also showed that the content of aromatics in the original hydrocarbons did not exceed 5 per cent. The original hydrocarbons were almost pure naphthenes having about 2.6 rings per molecule. The application of the Kurtz-Lipkin's method gives approximately 5.2 carbon atoms per ring,

i.e., the high molecular weight naphthenic acids investigated contain from 2 to 3 five carbon-atom rings per molecule. The almost pure naphthenic nature of the hydrocarbons regenerated contrasts with the results obtained by von Pilat and Müller.

Individual Fatty Acids

The petroleum acids from straight-run distillates were considered as true cyclic naphthenic acids. Shidkoff,⁷⁵ however, detected in petroleum some low molecular weight fatty acids as early as in 1893. Tanaka and Kuwata⁸¹ were the first to show that the petroleum acids from a Japanese gas oil contain some crystalline high molecular weight fatty acids: myristic, palmitic, stearic and arachinic. These acids amounted to 7.7 per cent of the total petroleum acid content. The separation was performed by lithium salts. In addition to these acids, there were some lower and higher homologs. Petroleum acids from some California and Borneo crude oils also contain palmitic acid.

Tschitschibabin and his co-workers^{85, 86} studied the petroleum acids of Baku crude oils and found fatty acids, particularly in low-boiling fractions. Cadmium salts were used for separating these from naphthenic acids. In the lowest fraction of petroleum acids isoamylacetic and diethylpropionic acids were detected. The fraction of the petroleum acids boiling between 215° and 218° consisted predominantly of fatty acids, whereas those above 260° (C₁₀-acids and higher) were mostly cyclic, *i.e.*, naphthenic. The fraction between 218° and 260° contained both classes of acids.

Holzmann and von Pilat⁴⁸ isolated high molecular weight fatty acids (myristic, palmitic, stearic and arachinic) from petroleum acids extracted from a spindle oil distillate (Boryslav crude oil, Poland). The petroleum acids were transformed into methyl esters which were fractionated. The free acids were regenerated from the fractions obtained and further purified by magnesium salts. Nenitzescu, Isacescu and Volrap⁶³ identified γ -methylvaleric and δ -methylcapronic acids in petroleum acids extracted from a Roumanian naphtha. δ -Methylcapronic acid corresponds to the isoamylacetic acid found by Tschitschibabin *et al.*

The following low molecular weight fatty acids were isolated by Hancock and Lochte⁸² from the sodium carbonate wash of a Signal Hill straight-run gasoline: formic, acetic, propionic, isobutyric, *n*-butyric, isovaleric, *n*-valeric, and dimethylmaleic. As might be expected, the fatty acids predominate among the acids present in this gasoline. Higher molecular weight fatty acids (*n*-heptanic, 2-methylhexanic, 3-methylhexanic, 4-methylhexanic and 5-methylhexanic) were identified in a California straight-run gasoline by Ney, Quebedeaux and Lochte.⁶⁶ Normal octanic and nonanic acids were reported by Wash *et al.*⁸⁷ Schulze, Shive and Lochte⁷⁴ found *n*-valeric, *n*-butyric, *n*-octanic and dimethylmaleic acids in the alkali wash of light burner oil.

Low molecular weight fatty acids are frequently present in cracked

distillates, apparently as decomposition products of naphthenic acids. Hall and de Taveau³¹ showed that naphthenic acids extracted from a gas oil and cracked at 815°F under a pressure of 200 lbs/sq. in. formed acetic acid. In addition to this experiment, the same authors found a series of fatty acids from formic to butyric in refinery waters of a Humble cracking plant. Williams and Richter³⁸ studied the petroleum acids extracted from the Dubbs cracking distillate from a West Texas gas oil. The acids were esterified, and the esters obtained were fractionated. The following acids were identified: isovaleric, *n*-heptanic, *n*-octanic and *n*-nonanic. No cyclic (naphthenic) acids were found. Orlov, Kasakova and Tschurbakov⁶⁷ analyzed petroleum acids from a Winkler-Koch pressure distillate; *n*-valeric, isovaleric and capronic acids were identified. In addition to these fatty acids, the pressure distillate contained some naphthenic acids from C₇ to C₁₂. This is a single indication of the presence of naphthenic acids in cracked products.

Individual Phenols

The methods of separation and identification of phenols developed for coal tars may be applied to petroleum phenols. Fractionation usually produces an incomplete separation and gives more or less narrow fractions containing several phenols. The same result can be achieved by fractional solution of phenols in dilute sodium hydroxide. The following chemical methods may be applied for fractional separation and identification:

(1) Sulfonation and subsequent regeneration of phenols from sulfonic acids by steam. The conditions of the sulfonation and regeneration differ for different phenols and may be selected for separation of individual phenols, as described for aromatic hydrocarbons in Chapter 3.

(2) Methylation of phenols with dimethylsulfate to phenylmethyl ethers and subsequent fractionation of the ethers.

(3) Bromination of phenols producing crystalline brominated phenols. The method is used to a limited extent because of numerous brominated compounds which may be formed. In some cases, however, the reaction gives predominantly one characteristic brominated compound.

(4) Condensation of phenols with monochloroacetic acid in the presence of alkalis producing crystalline aryloxyacetic acids and subsequent fractional crystallization of the acids.

(5) Condensation of phenols with phenylisocyanate producing crystalline uretans which are fractionally crystallized from an appropriate solvent.

A comprehensive survey of the above methods and literature data have been given by Agde and Kahles.⁹¹

The presence of phenols in minute amounts in crude oils and distillates has been known for a long time, but only in recent years have various phenols been identified in straight-run and cracked distillates. Tanaka and Kobayashi⁸⁰ detected a series of phenols in a Japanese kero-

sene distillate (Arita crude oil): three isomers of cresol, 1,3,4-xyleneol, 1,2,3-xyleneol, diethylphenol and triethylphenol.

Story and Snow⁷⁹ investigated the phenols present in straight-run and cracked distillates. Only traces of cresol were found in the alkali wash of a straight-run Mid-Continent gasoline and gas oil. Pressure distillates contained about 0.01 per cent of phenols; these were extracted, and the phenols produced were fractionated and identified. Carboic acid was absent, and all three cresols were present, as well as some higher homologs.

According to Nenitzescu *et al.*,⁸³ Roumanian straight-run gasoline contains more phenols than Mid-Continent products. The following phenols were identified: three isomers of cresol, 1,2,3- and 1,3,5-xyleneols. Phenol (carboic acid) was not found. The total percentage of phenols in this gasoline was not given, but they comprised about 10 per cent of the petroleum acids extracted from it.

In some cases the proportion of phenols, even in straight-run distillates, may be very high, as has been found by Holzmann and von Pilat⁴³ for a Boryslav petroleum distillate. The raw petroleum acids contained 28.9 per cent naphthenic and fatty acids and 24.7 per cent phenols. The following phenols were identified: three isomers of cresol, 1,3,5- and 1,3,4-xyleneols, β -naphthol, probably 1,2,4-xyleneol, and phenols with three methyl groups. Carboic acid was not found.

Williams and Richter⁸⁸ isolated a series of phenols from a West Texas pressure distillate. The petroleum acids obtained from it were esterified and the unreacted phenols were extracted by sodium hydroxide solution. The phenols recovered were fractionated and the following phenols were identified: carboic acid, orthocresol, paracresol, 1,3,5-xyleneol, and 1,2,4-xyleneol.

Schulze *et al.*⁷⁴ also detected carboic acid in the petroleum acids from an alkali wash of a Texas burner oil.

Potts and Morrow⁷² detected trimethylhydroquinone in a cracked distillate from a Texas crude oil.

Oxidation of Petroleum Products

Oxidation of petroleum hydrocarbons and oils may produce innumerable oxygen compounds, starting with alcohols or acids and ending with water and carbon dioxide. As a result of these processes, petroleum hydrocarbons are converted, more or less completely, into new products or new chemicals. All these reactions and chemicals are evidently beyond the scope of this volume. In other cases, petroleum products are oxidized and do not lose their identity and their character, as, for instance, cracked gasolines in storage or lubricating oils during active service. These processes, which take place under moderate conditions of oxidation, form products closely related to the hydrocarbons originally present.

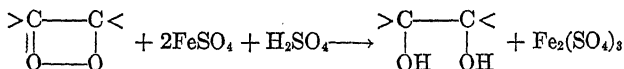
This chapter is confined to the oxygen compounds formed by oxida-

tion of petroleum hydrocarbons under the conditions prevailing during storage or operation. The oxidation of cracked gasolines and lubricating oils has been studied more thoroughly than of other products.

Determination of Oxidation Products in Cracked Gasolines.—There is an appreciable difference between cracked gasolines (and other cracked products) which are easily oxidized at room temperature and straight-run products which are oxidized slowly, particularly at moderate temperatures. This difference is evidently due to the chemical composition of cracked gasolines containing unstable and easily oxidizable unsaturates, while straight-run products (including lubricating oils) consist of more stable saturated hydrocarbons. In addition, the low-temperature conditions of oxidation of cracked gasolines in storage differ substantially from those of straight-run lubricating oils in operation. Thus, the oxidation products of cracked gasolines will be considered separately from those of straight-run products, such as lubricating oils.

No individual oxygen compounds have been isolated on oxidation of cracked gasolines. The so-called "dissolved gum" represents all the non-volatile oxidation products present in a cracked gasoline or, strictly speaking, all oxidation products which produce non-volatile compounds on evaporation. Another important group of oxidation products is the peroxides. The conventional method of determining peroxides by titration with potassium iodide in acidic solution cannot be applied to cracked gasolines due to the presence of unsaturates, which react with iodine.

According to Yule and Wilson,⁸⁹ the determination of peroxides in cracked gasolines is performed as follows. The content of peroxides is expressed in the so-called peroxide number, or in gram equivalents of active oxygen per 1,000 liters of gasoline. Ten cc of the gasoline to be tested are shaken with 50 cc of the standard water-acetone solution of ferrous sulfate in the presence of sulfuric acid and ammonium thiocyanate. The oxidation of ferrous sulfate by the peroxides proceeds according to the equation:



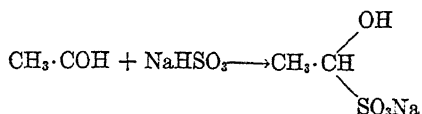
The ferric sulfate formed is titrated with 0.01*N* titanous chloride solution. The end point of the titration is marked by a change of color from red (due to ferric thiocyanate) to white.

Hock and Schrader⁴¹ recommend another method for determining peroxides. They reduce the peroxides by stannous chloride in acid solution, which is oxidized to stannic chloride. The excess of unreacted stannous chloride is determined by titration with ferric chloride with indigocarmin as indicator.

These authors did not recommend the Yule-Wilson method in view of the decomposition of peroxides catalyzed by the ferric sulfate formed in the reaction. Koch and Pohl,⁴⁹ however, found that the negative results obtained by Hock and Schrader are due to the use of tetralinperoxide,

which reacts differently and specifically, as compared with other peroxides. The conditions under which the most reliable results with the Yule-Wilson method are obtainable were discussed by Koch and Pohl.

Aldehydes and ketones formed on oxidation can be separated by the well known reaction with sodium sulfite; for example:



The crystalline double salt is treated with an acid to recover the aldehyde or ketone.

Dryer *et al.*²⁰ evaluated aldehydes colorimetrically by the intensity of the color imparted to rosaniline chloride discolored by sulfur dioxide.

The determination of dissolved gum is a standardized process. A 50-cc sample of cracked gasoline in a "Pyrex" dish (9 cm in diameter) is evaporated on a steam bath. An air jet is placed vertically over the dish at a distance of 4 cm from the initial surface of the sample. The hole in the air jet is $\frac{1}{16}$ inch and the air pressure is maintained at the equivalent of 2 cm of water. The dish with the sample remains on the steam bath 1 hour or more. The final drying is performed in an oven at 150°.

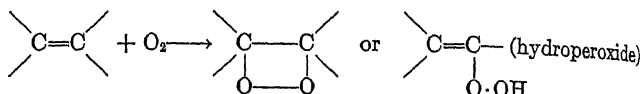
In another widely used modification of this method, an ethylene glycol bath is used instead of a steam bath, at a temperature of about 320°F. The time of evaporation is shortened to 8-14 minutes. The figures produced by this modification are close to those of the first modification on the steam bath, and are usually a little smaller.

Gum formation is accelerated not only at high temperatures but also in the presence of certain catalysts, such as copper, iron, and copper compounds. Thus gum formation and deposition are very rapid at 100° in a copper dish (copper dish gum test) or over iron tubing.

The determination of dissolved gum, important for the behavior of cracked gasolines in storage or in engines, has no chemical significance and may be considered as a bulk determination of the non-volatile compounds formed by the oxidation of unstable hydrocarbons.

The determination of peroxides, aldehydes, and acids by titration with adequate reagents gives only relative "numbers" which usually cannot be used even for an approximate calculation of the content of the above compounds. In some cases there is a substantial discrepancy even in the specification of the chemical character of the oxidation products. Story *et al.*,⁷⁸ for instance, found that the gum formed in cracked gasolines consists predominantly of acids which are saponified in alcoholic caustic solution. Dryer *et al.*²⁰ titrated the acids formed on oxidation of cracked gasolines by aqueous caustic solution and found that the gum is low in acids. Thus, so far very little is known of the nature of the oxidation products of cracked gasolines.

Oxidation Reactions in Cracked Gasolines.—The oxidation of cracked gasolines in storage is probably a chain reaction which starts with the addition of oxygen to the double bond, resulting in the formation of peroxides:



in which the olefinic unsaturation survives. For the sake of simplicity, the peroxide group is shown as being attached to one of the carbon atoms having a double bond, although actually the group may be attached to another carbon atom.

The peroxides may decompose with formation of more stable oxidation products, such as aldehydes, etc.; they may interact with other unsaturates yielding new oxidation products; or they may polymerize with formation of gumlike substances. The peroxides formed induce and catalyze further oxidation. The formation of peroxides from unsaturated hydrocarbons during recent years has been studied by Hock and his associates^{36-38, 40, 41} and by others.^{14, 21, 22}

Brooks⁸ was the first to show that the first stage of the action of oxygen upon unstable unsaturated hydrocarbons of cracked gasolines is the formation of peroxides. Even commercial refined cracked gasolines give a very marked positive test for peroxides upon exposure to air and sunlight for 30 minutes. The peroxides can be easily detected in the first weeks and months of the storage period. The peroxides formed catalyze the further oxidation of cracked gasolines. In the presence of water, dissolving peroxides, gum formation is considerably reduced.

Cassar¹¹ showed that the peroxides added to cracked gasolines actually catalyzed the gum formation. On the other hand, peroxidized gasolines may be "rejuvenated" or restored in the induction period after the caustic washing, removing peroxides formed.

Morrell, Dryer, Lowry and Egloff⁶⁰ oxidized cracked gasolines by oxygen at 100°C and confirmed that peroxides are the first products of oxidation. When the content of peroxides formed was sufficiently high, the gum content, both copper dish and air jet, increased to high figures. The same authors showed later that aldehydes and acids soluble in gasoline are formed in the more advanced stages of storage. The relative amount of peroxides, aldehydes and acids soluble in gasoline increases gradually with increasing time of storage. The gum begins to appear as soon as a considerable amount of peroxides has been formed and before any large formation of aldehydes and acids soluble in gasoline. Thus gum formation is closely related to peroxides.

Flood, Hladky, and Edgar²⁸ investigated the oxidation of various hydrocarbons at low temperatures, using the conditions of the standard tests. Most of the monoölefins are comparatively stable with respect to gum formation. At high concentrations, however, the oxidation of

monoolefins may be noticeable. Cyclic olefins with one double bond are less stable than open-chain olefins. The principal gum-forming hydrocarbons are aliphatic and cyclic diolefins and mono- or diolefins attached to the benzene ring. Of the diolefins, the conjugated hydrocarbons are very readily oxidized, while the hydrocarbons containing widely separated double bonds are much more resistant. The difference in the behavior of various hydrocarbons in oxidation is enormous. For instance, under the same conditions (100°C, 100 lbs pressure, 10 per cent concentration of the hydrocarbon in standard gasoline, 4 hours), pentene produced 0 mg of gum, 1-octene 0 mg, cyclohexene 0 mg, styrene 3,034 mg, 2,4-hexadiene 1,173 mg, and 1,3-cyclopentadiene 4,085 mg.

The gum-forming property of hydrocarbons is closely connected with the formation of peroxides. For instance, Hock and his collaborators^{37, 40} showed that cyclic olefins form peroxide much more easily than open-chain olefins. Cyclohexene formed 19 per cent peroxides for 200 hours at 30-40°C, while normal hexene under the same conditions gave only 0.4 per cent peroxides.

The oxidized compounds, including peroxides, may remain in solution and form the so-called "dissolved" gum, the determination of which has been described above. The dissolved gum remains in solution in gasoline until its concentration is comparatively low, not exceeding about 1,000 mg per 100 cc, or approximately 1 per cent by weight; otherwise, the gum is deposited on the walls or bottom of the container as a viscous liquid. Usually, however, gum deposition starts at much lower concentrations than this; 1,000 mg/100 cc should be considered the maximum amount of dissolved gum in gasolines. The deposition of gum, however, cannot be construed as the process of precipitation from a saturated solution; it is rather a chemical phenomenon related to the transformation of a soluble form of gum into an insoluble one.

At low temperatures gum deposition in storage is a process requiring several months, and can be detected after a long period, depending on the stability of the gasoline. The process is accelerated with increasing temperature. Determination of the induction period of oxidation of cracked gasolines takes place at 100° under 100 lbs/sq. in. cold pressure of oxygen, and results in the formation and deposition of gum in a few hours.

The dissolved gum can be obtained by evaporation of the gasoline. The gum remains as a residuum, usually as a sticky or semi-solid substance. This modification of the gum, however, is insoluble in gasoline, but is soluble in acetone and similar solvents.

The liquid deposit on the bottoms of containers and the semi-solid gum produced after the evaporation of cracked gasolines have about the same chemical composition. The gums consist of peroxides, aldehydes, ketones, and mostly acids. According to Story *et al.*,⁷⁸ the content of unsaponifiable matter in the gum is about 13-20 per cent, other constituents being saponifiable in alcoholic solution.

As mentioned above, the formation of dissolved gum with time indicates the induction period, after which oxidation and gum formation proceed rapidly. They are usually slow during the first months of storage (the induction period); then the rate of formation may suddenly increase, and oxidation will continue rapidly. In general, there is a close relation between the kinetics of peroxide and gum formation. Fig. 44

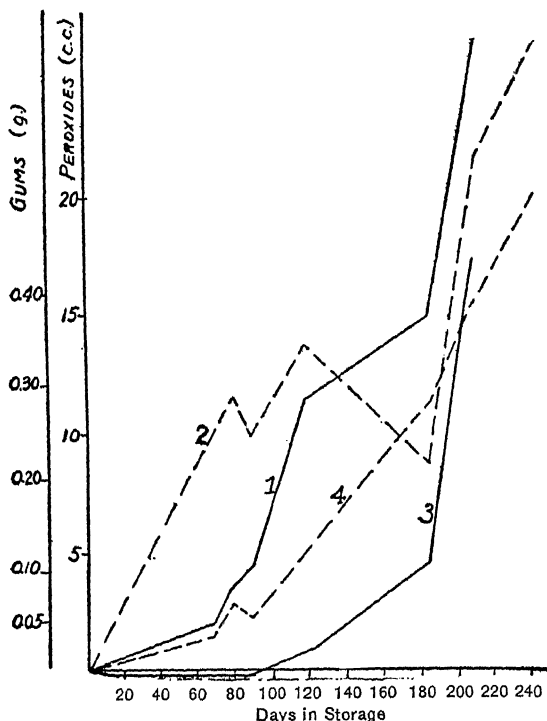


FIGURE 44. Formation of gums and peroxides versus time of storage. Curves: (1) gums in untreated cracked gasoline; (2) peroxides in untreated cracked gasoline; (3) gums in refined cracked gasoline; (4) peroxides in refined cracked gasoline.

illustrates this, according to the data of Pipik and Mezhebovskaia.⁶⁹ The increase of peroxides corresponds to that of gum content. A decrease in peroxides in certain periods of storage may be explained as a result of the vigorous conversion of peroxides to gum.

Content of Oxidation Products in Cracked Gasolines.—The formation and relative amount of oxidation products in cracked gasolines was investigated mostly for commercial mixed-phase and catalytically cracked gasolines. These data refer, however, only to the bulk determination of the oxidized compounds formed. In most cases the percentage of dissolved gum and in some cases that of peroxides, aldehydes and acids was determined.

Various types of synthetic gasolines differ greatly in their oxidation capacity, which is closely associated with unsaturation. Synthetic paraffins (alkylates) and hydrogenation gasolines are similar to straight-run gasolines and are extremely stable toward oxidation because of the absence of unsaturated hydrocarbons. Catalytically cracked gasolines are less stable than straight-run products, but much more so than thermally cracked gasolines. The stability of mixed phase-cracked gasolines is greater than that of vapor phase-cracked or polymer gasolines. This difference is due to the action of clay in catalytic cracking and of high pressures in the mixed-phase process, which effect polymerization and condensation of the most unstable unsaturates formed in cracking. The data of Table 105 show clearly that the oxidation stability of synthetic gasolines is closely related to the percentage of unsaturates.

The peroxide number of cracked gasolines varies from nil to 400 or more units. Velde¹¹² found that peroxide formation in cracked gasolines reaches 150-200 mg active oxygen per liter after one month of storage in sun light and 1000-1500 mg after 2 years of commercial storage. The use of inhibitors reduces peroxide formation. The peroxide number of commercial properly refined and/or inhibited gasolines does not exceed 5 to 10 units. A greater number indicates that the gasoline may be unstable in storage because of the catalytic effect of the peroxides on oxidation.

The chemical characteristics of the peroxides formed in cracked gasolines is entirely unknown. Diolefins seem to be more responsible for the formation of peroxides than other unsaturates, and thus the structure of peroxides may be closely connected with that of diolefins. Peroxides are formed, however, in cracking gasolines which contain monoölefins only.

Freshly distilled cracked gasolines do not contain gum because of its involatility. The formation of gum on oxidation in storage depends upon many factors, partially mentioned above: stability of gasoline, time of storage, temperature, presence of inhibitors, etc. The total content of oxidation products in cracked gasolines may vary in extremely broad limits from nil to such high figures as 1,000 mg or more per 100 cc of gasoline (dissolved gum). The content of dissolved gum in commercial cracked gasolines is usually small, not exceeding 10 to 15 mg/100 cc. A content above 15 mg is considered detrimental to the operation of engines. The permissible content of gum is controlled by proper refining and by the use of inhibitors.

Various fractions of cracked gasolines may differ substantially in their oxidation capacity and in gum formation, as has been found by Cassar,¹¹ Martin, Gruse and Lowy,⁵⁸ Mardles and Moss,⁵⁶ and Thomas.⁸⁴ The fractions boiling between 80 and 140° seem to be particularly rich in gum-forming hydrocarbons. According to Hock and Neuwirth,⁴⁰ the fractions boiling between 60 and 130° easily form peroxides.

Peroxides and gum present in gasolines decrease their efficiency by forming deposits in the fuel-feed tubing, carburetor and other parts of

the engine, as well as decreasing the octane number. Peroxides, being knock inducers, are particularly responsible for the last effect. Mardles and Moss⁵⁶ found that there is an approximate relationship between the loss in the octane number and the content of dissolved gum. A dissolved gum content of 100 mg may cause the loss of 7 octane units. The effect of peroxides on the octane number may vary within broad limits from 2 to 14 octane units per 200 mg of active oxygen per liter.^{110, 112}

The removal of peroxides from gasoline improves its octane number but does not restore it completely, indicating that the loss in the octane number is due not only to the presence of peroxides but also to other changes in the chemical composition on oxidation.

The data given above relate to the gum and peroxides formed on storage. The formation of gum on operation seems improbable, since the process is comparatively slow. The formation of peroxides, however, may be noticeable in engines at high intake temperatures, resulting in decrease in the octane number.¹⁰²

Oxidation Products of Straight-run Petroleum Oils

The oxidation of lubricating oils has been studied more thoroughly than that of other straight-run products because of the practical importance of this process, which deteriorates the lubricating properties of the oils. The oxidation of heavy residues for manufacturing so-called "blown asphalts" will be discussed in Chapter 9. The production of fatty and other acids by oxidation of paraffin wax and various oils has a lesser practical importance, particularly in the United States.

Oxidation of straight-run petroleum oils forms various products, such as peroxides, acids, alcohols, aldehydes, ketones, and resinous and asphaltic compounds. The analytical methods for quantitative separation and identification of various oxidation compounds are so far incomplete and inadequate.

Quantitative Determination.—The determination of oxidation products in straight-run products, particularly in lubricating oils, is widely used in commercial practice to evaluate the oxidation stability of the oils. The oil to be tested is oxidized under standard conditions at a given temperature for a specific time with a specific rate of air or oxygen in the presence or absence of catalysts. There are various modifications of the test, which differ in the above conditions.⁴⁵

The acids formed in oxidized oils are determined by titration with potassium hydroxide, as described for petroleum acids. The percentage of anhydrides and other saponifiable products is determined by reaction with an excess of 0.1*N* potassium hydroxide solution at boiling. The amount of unreacted potassium hydroxide is titrated with a 0.1*N* solution of sulfuric acid.

The condensation products formed on oxidation are determined mostly by precipitating with petroleum ether and centrifuging the precipitate (page 390). The methods of determining the relative amount of

oxidation products by titration or precipitation have mostly a conventional value. Only saponifiable compounds and substances insoluble in petroleum ether are determined by the methods in question; other compounds, such as aldehydes, alcohols, lactones and neutral resins, are not determined.

There is another, more important shortcoming of the conventional oxidation tests. The volatile products formed, such as carbon dioxide, water, low molecular weight acids, etc., evaporate more or less completely, particularly in the bubble tests, and thus are not determined. The quantity of volatile oxidation products may be very significant. From the practical standpoint, the low molecular weight acids formed may be much more corrosive than the high molecular weight acids which are titrated and determined in commercial tests.

Fenske, Stevenson, Rusk, Lawson, Cannon, and Koch²³ studied the oxidation of a series of commercial motor oils over the range 130 to 180°. Substantially all volatile and non-volatile oxidation products were determined. The main oxidation products are: water, carbon dioxide, and carbon monoxide, which on the average account for 60 per cent of the absorbed oxygen, water alone representing 50 per cent. Soluble saponifiable materials make up the average 25 per cent of the consumed oxygen, while fixed acids, volatile acids, and precipitable (by isopentane) products comprise the remainder. The proportion of volatile acids is usually greater than that of fixed acids. Neutral resins only partially precipitated by isopentane with asphaltenes and similar products were not accounted for. Hicks-Bruun *et al.*¹⁰¹ confirmed the above results and found that from 40 to 50 per cent of absorbed oxygen form water and carbon dioxide. The hypothetical reactions leading to the formation of these oxidation products were discussed. Kröger and Kaller¹⁰³ studied the oxidation of cetane and Larsen *et al.*¹⁰⁶ of numerous hydrocarbons which have given in general the same results as conventional lubricating oils. Larsen¹⁰⁵ found that lubricating oils derived from different crudes produce upon oxidation almost identical quantities of water and carbon dioxide; however, they show differences in the quantities of oil-soluble and oil-insoluble free and combined acids.

These investigations indicate that the determination of acidity and precipitable substances in conventional oxidation tests covers only a small part of the whole oxidation picture.

Another recommended method of investigating the oxidation of lubricating oils is the determination of oxygen absorbed or consumed on oxidation. This method does not differentiate the various classes of oxidation products formed, but does determine the total effect of oxidation. While the determination of various oxidation products involves a series of time-consuming operations, the method of oxygen absorption is much simpler and can be successfully used, at least for preliminary investigations. It has been used and described by Fenske and his co-workers²³ and by von Fuchs and Diamond.²⁷

Larsen¹⁰⁴ suggested evaluating the oxidation compound formed by the so-called Grignard reagent, *i.e.*, methyl magnesium iodide. The oxygen compounds with active hydrogen, such as water, alcohols and acids, react with it to form methane, the volume of which is measured. Other oxygen compounds also react, but without evolution of methane. The total oxidation effect is measured by the consumption of the reagent.

Separation of the oxidation products in oils can be accomplished by various methods. The low molecular weight acids and other volatile compounds can be removed from the oil by distillation up to a suitable temperature. The high molecular weight acids formed can be extracted with sodium- or potassium-hydroxide solutions. The solutions of soaps formed are then treated with ether or benzene to remove the hydrocarbons emulsified in the soap solutions. This operation, even repeatedly performed, may not remove the hydrocarbons completely. The soap solution freed of hydrocarbons is decomposed with hydrochloric acid to liberate high molecular weight acids insoluble in water. The acids, washed and dried, may be treated further with a petroleum naphtha to separate the acids soluble in naphtha (mostly high molecular weight mono-acids) from those which are insoluble (mostly hydroxy-acids). It can hardly be expected, however, that this separation would be complete.

The separation of hydroxy-acids insoluble in naphtha may interfere with the precipitation of asphaltogenic acids, which are also insoluble in naphtha. Marcusson and Bauerschafer⁵⁴ used naphtha for separating asphaltogenic acids from other acids produced by the oxidation of transformer oils and white oils. The mixture of hydroxy-acids and asphaltogenic acids insoluble in naphtha may probably be separated with such solvents as benzene, which dissolve asphaltic compounds. Hydroxy-acids can be separated with concentrated sulfuric acid, which dissolves the hydroxy-acids but not the carboxylic acids. Dovankov¹⁹ used both sulfuric acid (or hydrogen chloride) and naphtha for a more complete separation.

Treatment with solvents frequently permits separation not only of acids but also of other oxygenated compounds, because they are more soluble than are hydrocarbons. Any solvent may be used under suitable conditions, but liquid sulfur dioxide and isopropyl alcohol are particularly recommended. The acids may be separated from the extract by treatment with sodium- or potassium-hydroxide solutions from non-saponifiable oxidation products (including neutral resins and asphaltenes) contaminated with hydrocarbons.

As in the case of naphthenic acids, the esterification of acids formed on oxidation into methyl esters, followed by vacuum fractionation of the esters, may be of use for separating acids.

Such oxidation products as anhydrides or lactones can be separated by saponification with a 1.0*N* solution of potassium hydroxide by boiling under reflux, after the free acids have been extracted with cold potassium hydroxide solution. The alkaline solution of saponified compounds is

treated with ether or benzene to remove emulsified hydrocarbons, and then is acidified to liberate free acids from anhydrides and lactones.

Aldehydes and ketones formed on oxidation can be separated by reaction with sodium bisulfite solution and then recovered from the extract by acidification. It is not known, however, how completely this method separates high molecular weight aldehydes and ketones.

Larsen *et al.*¹⁰⁸ determined the total amount of carbonyl groups (aldehydes and ketones) by reaction with hydroxylamine hydrochloride to form oximes and an acid which is titrated.

Alcohols, if formed, can be separated from other neutral oxidation products by esterification. Boric acid is frequently used for this purpose. Shorygin and Makarov-Zemliansky¹¹¹ esterify alcohols with boric acid in the presence of an excess of benzene (8 volumes) on a water bath. The water formed is distilled off, together with benzene. After the benzene is removed, the distillation is continued *in vacuo* to remove the unreacted constituents. The residuum consists of boric acid esters and is hydrolyzed by a conventional method to liberate alcohols.

The separation of neutral resins and asphaltenes from other oxidation products can be carried out after acid separation and saponification. The oil, free of these compounds, is treated with an excess of petroleum ether to precipitate asphaltenes. In the filtrate the neutral resins are appropriately adsorbed, as will be described in Chapter 9.

The determination of neutral resins in oxidized oils is much more important than that of "insolubles" in petroleum ether, widely used in commercial tests. Haus,³⁵ and Davis *et al.*¹⁵ pointed out that the quantity of neutral resins in the initial stages of oxidation may be many times greater than that of "insolubles." The authors determined by adsorption the total amount of neutral resins and acids, including the saponifiable compounds, without preliminary separation of acidic compounds.

As in the case of gum formed in cracked gasolines, the oxidation products of heavy oils so far have not been identified, with the exception of low molecular weight acids, aldehydes, etc. Usually only the total effect of oxidation, expressed in terms of acids, resins, etc., was determined. The chemical structure of individual oxidation compounds remains entirely obscure.

Oxidation Reactions.—Many attempts have been made to investigate the mechanism of the oxidation of petroleum oils, particularly of lubricating oils, and various theories, including the peroxide or hydroxylation theories, have been advanced, without conspicuous success. It is not believed that the unique oxidation mechanism can be applied to all hydrocarbons composing petroleum oils. The mechanism of oxidation of paraffins or paraffinic side chains may be different from that of aromatic or naphthenic rings, etc. Even the oxidation of an individual naphthene with a paraffinic side chain may have two different sets of reactions, one for the side chain and another for the nucleus. Fenske *et al.*²³ actually observed, for instance, that the oxidation curves of highly paraffinic

lubricating oils differ substantially from those of oils rich in aromatics, as will be seen later.

Another interesting observation along this line has been made by Pardun and Kuchinka.^{67a} The temperature coefficient of the oxidation of paraffin wax by air at temperatures from 110 to 140° was found to be constant and equal to 2.52. Above that range it decreased to 1.7-1.8, indicating two different oxidation mechanisms, one at the lower and the other at the higher temperature.

The formation of peroxides on oxidation of unsaturates is considered as the first stage in the oxidation of cracked gasolines. The formation of peroxides can occur also on oxidation of saturated hydrocarbons, including the high molecular weight hydrocarbons of lubricating oils; but the mechanism of these reactions, its extent, and the part played by the peroxides formed are unknown. According to Medvedev,¹⁰⁸ however, peroxides are formed as primary products on oxidation of saturated hydrocarbons.

Chavanne and co-workers⁹²⁻⁹⁸ were the first to study systematically the formation of peroxides by saturated hydrocarbons, paraffins, and particularly naphthenes.

Mondain-Monval and Quanquin⁵⁹ obtained peroxides on oxidation of normal paraffins from hexane to octane at about 325°; and Ivanov⁴⁴ found that peroxides are readily formed on oxidation of cyclohexane at 316 to 370°. Hock and Lang³⁹ and Hock and Susemihl⁴² investigated the peroxide formation on oxidation of tetralin, indene and benzene homologs. According to George, Rideal and Robertson,²⁸ oxidation of alkylbenzenes gives peroxides in the amount of 60 to 80 per cent of the oxygen absorbed. The peroxides of long-chain paraffins are less stable and are detected on oxidation in small quantities only. Plissoff⁷⁰ studied the oxidation of paraffin wax and determined the amount of peroxides formed; it increases to a maximum in the beginning of oxidation, and then decreases to the vanishing point, while the formation of other oxidation products gradually progresses.

Dornste and his co-workers observed the formation of peroxides on oxidation of white oils,¹⁶⁻¹⁸ but no peroxides were detected on oxidation of other less refined oils. Other oxidation products of saturated hydrocarbons and straight-run petroleum products, particularly acids, have been studied more thoroughly.

Oxidation of petroleum wax or long-chain paraffin hydrocarbons at moderate temperatures (from 100 to 150°) produces fatty acids, hydroxy-acids, as well as anhydrides, lactones, aldehydes, alcohols, etc. Some low and medium molecular weight acids, such as formic or C₃-C₁₀ acids, are also formed as a result of oxidation and decomposition. Neutral oxidation compounds of low and intermediate molecular weights, from C to C₁₂, etc., are also formed. Nametkin and Zworykina¹⁰⁹ and Mannes¹⁰⁷ summarized the results obtained on oxidation of paraffin wax. The process may be noncatalytic or catalytic in the presence of known

oxidation catalysts. The oxygen pressure is a beneficial factor in producing a high yield of fatty acids. Under favorable conditions, this yield may be as high as 40 per cent or more per pass, the remainder being mostly unchanged paraffin hydrocarbons. Higher yields are not recommended, since advanced oxidation is accompanied by decomposition of the acids formed. The formation of resins and asphaltic materials is negligible.

Fischer and Schneider²⁵ found that the oxidation of paraffin wax produces fatty acids with an odd number of carbon atoms, such as $C_{13}H_{26}O_2$, $C_{15}H_{30}O_2$, $C_{17}H_{34}O_2$, $C_{19}H_{38}O_2$. The acids are different from the well known high molecular weight fatty acids, such as palmitic or stearic, and apparently have an iso-structure.

The formation of acids containing naphthenic or aromatic rings is an important process in the oxidation of high-boiling oils, such as lubricating or transformer oils. The long paraffinic side chains of the cyclic hydrocarbons of such oils are oxidized at moderate temperatures, forming acids, which render the oils acidic and corrosive.

According to Burwell,¹⁰ the mechanism of oxidation of long paraffinic chains is as follows. The first stage leads to the formation of an alcohol in α or β position. The end CH_3 group is not attacked. In the second stage the alcohol forms a ketone which, on further oxidation, accompanied by breaking of the chain, gives two acids: a high molecular weight fatty acid and formic or acetic acid. Thus the former will contain one or two carbon atoms less than the original chain.

The mechanism of Burwell may explain the formation of low molecular weight acids on oxidation of high molecular weight paraffins, but it seems insufficient to clear up the oxidation picture. In contrast to Burwell's data, Pope, Dykstra and Edgar²¹ found that vapor-phase oxidation of *n*-octane and isomeric octanes at 250 to 500° attacks the methyl group of the *n*-octane and also the methyl group at the end of the longest free straight chains.

It is important to point out that the formation of fatty acids is closely related to the length of the paraffinic side chains. The long ones are oxidized much more readily than the short, just as high molecular weight paraffins are oxidized more readily than, for instance, methane or ethane. Thus, the oils produced from paraffin-base crudes, containing cyclic hydrocarbons with long paraffinic side chains, are more susceptible to this type of oxidation than those obtained from naphthenic or asphaltic crudes. In addition to the oxidation of end groups or groups close to the end, cracking of paraffinic side chains on oxidation takes place to some extent at various points, resulting in the formation of acids and other oxidation products of different molecular weights.

The formation of hydroxy-acids, which are insoluble in petroleum oils, may be of importance in the production of the so-called sludge, which is partially saponifiable. It is probable that the acid constituents of the sludge are at least partially of the hydroxy variety. Hydroxy-

acids are formed mostly in the advanced stages of oxidation. Thus, their formation may be controlled to a certain extent by the duration of oxidation.

As in the case of paraffin wax, the oxidation of high-boiling oils may yield, in addition to acids, various other oxidation products, such as peroxides, aldehydes, ketones, anhydrides, etc., at least under more moderate temperature conditions.

There are other oxidation reactions which readily occur when high-boiling oils are exposed to the action of oxygen, and which attack the rings of naphthenes, particularly polycyclic aromatic hydrocarbons. The mechanism of these reactions is not too clear. The first stage is probably partial oxidation of certain more unstable rings, followed by condensation of the oxidized rings to more polycyclic structures. Some of these reactions are discussed in Chapter 9.

Neutral resins and asphaltenes are formed in the advanced stages of condensation while the acids may be entirely absent. This type of oxidation of high-boiling oils results in increase in viscosity, and thickening and asphaltization of oils; it predominates in highly aromatic oils. The formation of asphaltic substances is frequently specified as the sludging due to the accumulation of sediment. Hicks-Bruun *et al.*¹⁰¹ found that the increase in viscosity on oxidation of lubricating oils is due mostly to the neutral resins formed. The peptizing effect of neutral resins and aromatic constituents on the asphaltenes and carboids formed on oxidation of lubricating oils should not be overlooked. As has been pointed out recently by Faust, residual oils at high operating temperatures produce asphaltenes and carboids which are peptized by resinous constituents and convert lubricating oils into asphaltic systems. On the other hand, the asphaltenes and carboids formed in distillate lubricating oils poor in resins are segregated as heterogeneous particles not affecting substantially the viscosity and microstructure of lubricating oils.

Fenske, Stevenson, Lawson, Herbolsheimer and Koch²⁸ studied various fractions produced from a Pennsylvania distilled lubricating stock by fractionation and solvent extraction. The fractions, containing 80 per cent or more of paraffinic side chains and no aromatic rings, give the inhibited or autocatalytic oxygen absorption (*i.e.*, oxygen absorbed versus time). Such curves have induction periods during which the rate of oxidation is either nil or very low. The formation of various acids is great in this type of oxidation, and a small amount of oil-insoluble substances are formed. Another type of oxidation is characteristic of the fractions containing a large proportion of aromatic rings (up to 40 per cent) and a correspondingly lower proportion of paraffinic side chains than the first type. The oxygen absorption curves for these oils are almost straight lines. The formation of acids is much less than in oils of the first type, whereas the formation of oil-insoluble substances is considerable. Thus, speaking very generally, the oxidation results correspond more or less to the chemical structure of the fractions, paraffinic

chains producing mostly acids and aromatic rings mostly condensation products. This parallelism between the oxidation products of lubricating oils and their chemical composition, however, cannot be expected to be strictly accurate, as many other factors affect oxidation; these will be discussed later.

Some authors postulate that the formation of such compounds as aldehydes, ketones, and acids is a prerequisite for the formation of resins and asphaltic substances. Broadly speaking, this point of view is contradictory to the well known fact that the formation of neutral resins and asphaltenes by oxidation of residues is a predominant process, not accompanied to an appreciable extent by formation of other oxygen compounds. On the contrary, the oxidation of paraffin waxes under moderate temperature conditions produces mostly acids and no asphaltic substances. These results are apparently due to the different chemical nature of the residues, which are predominantly of cyclic structure, and of paraffin waxes which do not contain any cyclic hydrocarbons.

On the other hand, the formation of asphaltic products, "lacker" or sludge from acids and similar oxidation products is quite probable in the advanced stages of oxidation, particularly in the presence of polycyclic hydrocarbons. It is well known that highly refined (over-refined) oils very easily build up acids on oxidation. In the first stage of the oxidation sludge does not form. In a more advanced stage it does form, frequently with a decrease in acidity. In such cases the formation of asphaltic compounds as a result of the condensation of acids, probably with polycyclic naphthenes, is unquestionable. Thus in such oils the formation of acids precedes the formation of sludge. In the first stage the sludge formed may consist largely of acids insoluble in oils, which are gradually transformed into resins and asphaltic substances.

The formation of acids as a preliminary stage for producing resins and asphaltic compounds has been advanced by Marcusson.⁵³ Later Marcusson and Bauerschafer⁵⁵ accepted acids, resins and ketones as primary oxidation products. Haslam and Frolich³⁴ suggested that the formation of aldehydes and ketones precedes that of asphaltic substances.

There is an interesting interrelation between these two processes of acid and asphalt formation. It has been mentioned that oils highly refined by solvent treatment or by sulfuric acid and free of resins and polycyclic aromatic hydrocarbons are particularly likely to form acids on oxidation. Thus the degree of oxidizability of petroleum oils depends upon the degree of the treatment or refining. In general, treatment with sulfuric acid or solvent increases the stability of the oil toward oxidation, because the easily oxidizable substances are thus removed. However, excessive treatment with solvent or sulfuric acid usually decreases the stability with respect to acid formation. On the contrary, the formation of asphaltic products on oxidation is very low in such over-treated oils.

If the formation of acids is a chain reaction, like the oxidation of unsaturates, it is possible that the unstable aromatic hydrocarbons and

resins break the chain, being oxidized or forming some unstable compounds with initial oxidation products of paraffinic side chains. Thus the aromatic hydrocarbons, resins, and possibly other oxygen and sulfur compounds play the part of natural inhibitors in oils. The suppression of sludge formation or asphaltization in lubricating oils is a comparatively easy problem: removal of asphaltenes, resins, and unstable aromatic polycyclic hydrocarbons produces the desired effect. Any treatment of lubricating products with sulfuric acid, clay, or solvent greatly reduces the sludging or asphaltization of lubricating oils. The suppression of the formation of acids is much more difficult because the paraffinic side chains of cyclic hydrocarbons, which are responsible for this phenomenon, are not affected by the above treatments. In addition, it should be kept in mind that long paraffinic side chains are an important asset of lubricating oils, causing high values of viscosity and viscosity index. Moreover, as stated above, over-refining brings about an increase in the acid-forming properties by removing natural inhibitors.

Thus, the use of various artificial inhibitors may be beneficial for suppression of acid formation in lubricating oils. Oxidation inhibitors in such oils are being used extensively at present.

The effect of individual aromatic hydrocarbons and aromatic fractions on the oxidation of lubricating oils has been studied by Fuchs and Diamond.²⁷ They oxidized highly refined oils in the presence of varied amounts of aromatics. The total amount of oxygen absorbed was determined under identical conditions of oxidation (temperature and rate of oxygen). As might be expected, the highly refined oil oxidized rapidly. The addition of an aromatic improved its oxidation stability to a certain concentration of the aromatic, at which it had maximum stability. A further increase of the concentration of the aromatic decreased the stability and correspondingly was accompanied by increasing consumption of oxygen. Thus the oil most stable to oxidation should contain an optimum amount of natural or added aromatics.

These results show that the oxidation of aromatics is a process independent of the oxidation of naphthenes and paraffinic side chains. In low concentrations the aromatics retard the oxidation of saturated hydrocarbons, oxidation of the aromatics themselves being an insignificant factor. At higher concentrations, oxidation of the aromatics is superimposed on that of saturated hydrocarbons and may reverse the retarding effect of oxidation.

The same authors studied the oxidation of neutrals prepared from the same stock but with a different content of natural aromatics. The specific dispersion of these neutrals varied from 103 to 117.5. On the average, in this range of aromaticity the degree of oxidation was maximum for an oil of specific dispersion 103, and gradually decreased for more aromatic oils.

The effect of natural sulfur compounds of lubricating oils on oxidation has been studied by Denison.⁹⁹ He removed the sulfur compounds

by treating lubricating oils for several hours at 500°F with metallic sodium under 200 lbs/sq in hydrogen pressure. The oxidation stability decreased markedly after the treatment, indicating that the sulfur compounds are natural inhibitors of oxidation. Sulfur-free lubricating oils easily form peroxides on oxidation. If sulfur compounds are added to an oil containing peroxides, the peroxides reacting with the sulfur compounds are rapidly reduced. Thus the sulfur compounds control the formation of peroxides.

It should be pointed out, however, that the sulfur in high-boiling oil fractions is usually associated with oxygen, as, for instance, in neutral resins to be discussed in Chapter 9. The removal of sulfur by metallic sodium used by Denison should destroy not only sulfur compounds but oxygen and sulfur-oxygen compounds as well. Consequently, the inhibiting effect observed may be due to the combined action of sulfur, oxygen, and sulfur-oxygen compounds present in lubricating oils.

There are widely different opinions on the part played by natural inhibitors in the oxidation of lubricating oils. An extreme point of view has been recently developed by Larsen *et al.*¹⁰⁶ to the effect that "oxidation stability of a lubricating oil results not from the stability of basic hydrocarbons but from content of natural inhibitors." The same authors found, however, that naphthalene homologs and some other polycyclic hydrocarbons are particularly stable upon oxidation as compared with other hydrocarbons. This discrepancy is explained by the assumption that the oxidation-stable hydrocarbons rapidly form very efficient inhibitors on oxidation.

Thus the behavior of lubricating oils on oxidation is a complex phenomenon because of the fact that different oxidation reactions may be involved in the process. The inhibiting effect of certain hydrocarbons and compounds is an additional complicating factor. The conditions of oxidation, such as temperature and catalysts, are another powerful factor affecting the results. It should be clearly emphasized that the conditions of oxidation may influence the ultimate result to a greater extent than the chemical nature of the oils themselves. Larsen and Armfeld⁵² showed clearly that the order of stability of three lubricating oils (Pennsylvania, Mid-Continent and California) very different in chemical composition may be changed at will by varying the concentration of a copper catalyst dissolved in them.

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Chapter 8

Sulfur and Nitrogen Compounds

Sulfur Compounds in Petroleum

The sulfur compounds present in petroleum belong to various classes, including inorganic compounds, mercaptans, aliphatic sulfides, cyclic sulfides or thiophanes, disulfides, and thiophenes. Petroleum resins and asphaltic compounds containing oxygen and sulfur will be discussed in the following chapter. In addition to the compounds mentioned above, refined oil products may contain polysulfides, sulfonic acids (or corresponding salts), and esters of sulfuric acid, which are absent in original products and which are formed as a result of treating processes.

It should be pointed out that, in addition to the above classes, some other sulfur compounds may exist in petroleum. As will be seen later, the determination of such compounds in gasolines and kerosenes gives a considerable proportion of so-called "residual" sulfur compounds, which includes some thiophenes. It is quite probable, however, that, in addition to the latter, other so far unknown classes of sulfur compounds are represented in this group. The presence of polycyclic sulfur compounds in high-boiling distillates has been discussed by Challenger.¹⁸

The origin of the sulfur compounds mentioned above is not quite clear. Resinous and asphaltic constituents containing sulfur and oxygen are undoubtedly present in virgin crude oils. The formation of free sulfur, hydrogen sulfide, and mercaptans may frequently be observed on distillation, as a result of the decomposition of some unstable, unknown sulfur compounds. This does not mean, however, that all low molecular weight sulfur compounds, such as mercaptans, sulfides, etc., are decomposition products, as believed by some authors. It should be remembered that hydrogen sulfide and mercaptans are present in some oil-field gases and also may be the constituents of virgin crudes.

The ultimate origin of sulfur compounds in crude oils lies at least partially in the organic material from which the crudes originated. On the other hand, the possibility of a reaction of crude oils with sulfates *in situ* should not be overlooked. The reaction is substantially the oxidation of hydrocarbons and reduction of sulfates to sulfides, which may react further with hydrocarbons to form various sulfur compounds. Sulfates are frequently present in the clays, sands and waters associated with the crude oils. It is of interest that oil-field waters are usually rich in chlorides but do not contain sulfates in any appreciable quantities. Oil-field waters originated from the sea water buried with the plants and

animals from which petroleum was formed; thus they contained chlorides as well as sulfates. Accordingly, the reactions of desulfurization of inorganic sulfates with the hydrocarbons of crude oils, leading to the formation of sulfides and probably to some organic sulfur compounds, seem highly probable. In addition, pyrites and similar sulfides, if present, may also react with hydrocarbons with formation of organic sulfur compounds.

The separation and determination of various sulfur compounds in petroleum oils is a difficult problem, particularly for high-boiling distillates. The present knowledge of sulfur compounds in petroleum is limited mostly to gasolines and naphthas.

Determination of Total Sulfur Content

The total content of sulfur compounds in crude oils and oil products can be approximately evaluated by determining the sulfur content. In the case of volatile distillates, this is usually found by the lamp method, *i.e.*, by complete combustion of the sample and by determination of sulfur dioxide in the combustion products (ASTM method D 90-34 T). The modifications of the lamp method have been described by Edgar and Calingaert²³ and Schulze, Wilson and Buell.⁶⁸ Korb and Cornelius⁴⁰ applied the lamp method to the determination of sulfur in lubricating oils by dilution of the oils to be tested with naphtha in the proportion of 1:3 by weight.

The method of Ter Meulen and Hesling³⁸ or its modifications can be applied to volatile and non-volatile products. The combustion of the sample to be tested takes place in a current of air in a quartz tube filled with quartz beads. The product is placed in a pipette and gradually released to the tube, which is heated to red heat. The combustion products are passed to an absorption apparatus containing an oxidizing solution, *e.g.*, hydrogen peroxide in aqueous solution. As a result, the sulfur of the oil is converted to sulfuric acid, which is determined in the conventional manner. The amount of oil to be analyzed by this method, as well by the lamp method, may vary within broad limits, depending upon the percentage of sulfur. Thus, the methods in question can be applied to any product either rich or poor in sulfur.

The total sulfur content can also be determined by combustion of a weighed amount (about 1 gram) of the product in an oxygen bomb. The combustion takes place in the presence of water (about 20 cc). The sulfur is oxidized to sulfur dioxide and trioxide, which are dissolved in the water. The pressure in the cooled bomb is gradually released, and the contents washed with water into a beaker. The aqueous solution is further oxidized completely to sulfuric acid either by sodium peroxide or bromine (in the presence of hydrochloric acid). The sulfuric acid formed is determined as barium sulfate.

This method can be used for oils containing not less than 0.1 per cent of sulfur. Various modifications of this method are known. It is under-

stood that the same method can also be applied to light distillates with the exception of those that are too volatile. The Carius method, *i.e.*, the complete oxidation of a weighed amount, from 0.2 to 0.3 gram, of a petroleum product by nitric acid also gives very reliable results. This method is feasible only with petroleum products containing not less than 1 per cent sulfur. Otherwise the quantity of sulfuric acid formed is too small for accurate determination. The increase in weight of the product is prohibitive in view of the high pressures.

For non-volatile products, the determination of total sulfur can be performed by the method of Eschka or Pringsheim with a moderate degree of accuracy.

Eschka's method: One gram of product, thoroughly mixed with 1.5 grams of a mixture of 2 parts magnesia and one part soda, is heated in a platinum crucible to red heat. The crucible should be placed at a slant to facilitate access of air. Total combustion requires about 1 hour. The sulfur present in heavy oil is combined with sodium and magnesium. The contents of the crucible are oxidized in a beaker with bromine water and nitric acid under heating. The sulfuric acid formed is determined as barium sulfate.

Pringsheim's method: A mixture of 0.2 gram of an oil and an 18 fold amount of sodium peroxide in a steel crucible is ignited by an iron wire heated to red heat. The reaction product is dissolved (carefully) in water, acidified with hydrochloric acid, and precipitated with barium chloride.

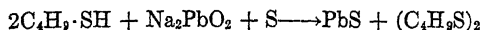
Determination of the total sulfur content for rather narrow fractions may give approximate figures of the content of sulfur compounds present, the molecular weight of which can be evaluated.

Determination of Free Sulfur

Free sulfur in petroleum is frequently removed by the conventional reaction with metallic mercury as mercuric sulfide. In gasolines and kerosenes the total amount of sulfur is determined by the lamp method before and after the removal of free sulfur. The difference equals the amount of free sulfur. This conventional method, however, is not reliable in the presence of mercaptans. Bell and Agruss⁸ and Schindler, Ayers and Henderson⁶⁷ showed that the mercuric sulfide formed by the reaction between mercury and free sulfur adsorbs mercaptans, resulting in low values for mercaptan sulfur content. Thus, it is recommended that the mercaptans in the original gasoline be determined, ignoring the free sulfur which may be present. Brown¹⁷ also found that the removal of free sulfur with metallic mercury in the presence of mercaptans gives too high values for free-sulfur content and too low values for mercaptan sulfur. He recommended removing the free sulfur by treatment with a 3 per cent solution of sodium sulfide (see later) and determining the total sulfur content by the lamp method before and after the treatment.

Wirth and Strong⁸⁴ recommended removing free sulfur by adding a

known amount of butyl mercaptan to the gasoline to be tested in the presence of litharge and sodium hydroxide. The free sulfur reacts according to the equation:



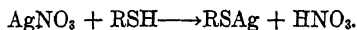
and is converted into lead sulfide. The amount of mercaptan sulfur is determined by titration with silver nitrate before and after the treatment, and the loss in mercaptan sulfur divided by two gives the amount of free sulfur. This method gives very reliable results, as has been confirmed recently by Ball.⁷

Determination of Hydrogen Sulfide and Mercaptans

The determination of hydrogen sulfide is carried out by reaction with acidified cadmium chloride, which does not react with mercaptans. The sample is shaken for 2-3 minutes, with acidified CdCl_2 solution made by adding 10 grams of CdCl_2 to 100 cc of water, to which 1 cc of concentrated HCl is subsequently added. This quantity of acid prevents the formation of cadmium mercaptides. The cadmium sulfide formed is filtered and washed.

Another method of quantitative removal of hydrogen sulfide is by treatment with sodium bicarbonate (of about 10 per cent), which reacts completely with hydrogen sulfide and does not attack mercaptans.

The determination of mercaptans is based on the formation of mercaptides with heavy metals, as, for instance,



The mercaptan content is usually calculated on the basis of sulfur in the form of mercaptans.

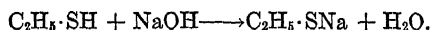
Borgstrom and Reid¹⁴ titrate mercaptans with an excess of 0.05*N* silver nitrate. The excess of silver nitrate is titrated with ammonium thiocyanate in the presence of iron alum. If hydrogen sulfide (giving the same reaction) is present, it is first removed by acidified CdCl_2 solution, which does not react with mercaptans. An alternative method is to remove mercaptans by silver nitrate and to determine the total sulfur by the lamp method before and after removal. The authors point out, however, that silver nitrate may possibly not react with some mercaptans and that it may react with other sulfur compounds. Malisoff and Anding⁵⁰ slightly modified the method described using 0.005*N* silver nitrate, standardizing the ferric alum indicator, etc. Tamele and Ryland⁷¹ and Davies and Armstrong¹⁸ use the same reagent for titration of mercaptans, but determine the end point potentiometrically with a silver electrode. The method is applicable to colored solutions.

Copper sulfate can also be used for titration of mercaptans. Approximately 0.01*N* solution of copper sulfate in sodium hydroxide and ammonia is used. The titration proceeds until the solution retains its blue color. Bond¹² employs a standard solution of cupric oleate in kero-

sene instead of copper sulfate in aqueous ammonia. The end point of the titration is marked by a green tint in the gasoline.

Removal of Sulfur Compounds with Sodium Hydroxide

Hydrogen sulfide and mercaptans are the only sulfur compounds present in oils which react with sodium or potassium hydroxide solutions, forming sulfides and mercaptides which are soluble in the reagent, for instance,



The separation is complete, however, only for hydrogen sulfide and low molecular weight mercaptans from methyl to propyl. Higher molecular weight mercaptans react only partially with alkaline solutions, and as a result the separation is incomplete. This may be due to the hydrolysis of high molecular weight mercaptides (the above reaction is reversible), or to the insolubility of mercaptans in aqueous sodium hydroxide solution. Yabroff and co-workers⁸⁸ showed that the removal of mercaptans boiling in the range of gasolines may be complete in the presence of certain reagents, *i.e.*, solutizers, which increase the solubility of mercaptans in the aqueous phase and prevent the salting-out effect of sodium hydroxide. This reaction with solutizers apparently can be used for separation of high molecular weight mercaptans. The removal of mercaptans with alkaline solutions is extensively used for gasolines. Little is known of the reaction between high molecular weight mercaptans, which may be present in kerosenes or gas oils, and alkaline solutions. It is understood that the alkaline treatment of kerosene or gas oil also extracts naphthenic acids, as described in Chapter 7.

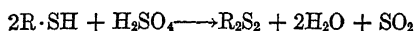
Separation of Thiophenols

Thiophenols belong to the class of mercaptans and are removed with phenols and acids by treatment with sodium hydroxide solution. Since the acidity of thiophenols is greater than that of aliphatic mercaptans of the same molecular weight, the removal of thiophenols is more complete than in the case of aliphatic mercaptans. Some cracked gasolines contain mostly phenols and thiophenols. The proportion of thiophenols in cracked naphthas is comparatively high, frequently amounting to 20 per cent of the total phenols and thiophenols. As the properties of these two products are very similar, their separation is not an easy task. Thiophenols are on the average slightly more acidic than phenols. Thomas and Cummings⁷⁴ suggested a method, based on this difference, which permits a separation. Phenols and thiophenols are extracted from a distillate with sodium hydroxide solution and then are liberated by acidizing. The resulting "acid oil," containing both phenols and thiophenols with some emulsified hydrocarbons, is dissolved in a suitable solvent, *e.g.*, diisopropyl ether. The solution is extracted with normal sodium hydroxide solution in an amount insufficient for complete neu-

tralization of the phenols and thiophenols. Under these conditions, the latter are converted into thiophenolates and removed with sodium hydroxide solution, whereas the phenols remain in the ether. The method is commercial, and the separation is by no means quantitative. The thiophenols separated contain about 80 per cent pure thiophenols.

Separation of Sulfur Compounds with Sulfuric Acid

Strong sulfuric acid *per se* is not selective with respect to sulfur compounds reacting vigorously with unsaturated and aromatic hydrocarbons; it oxidizes mercaptans to disulfides according to the equation:



The reaction, however, takes place only in the presence of an excess of sulfuric acid.

Other low and medium molecular weight sulfur compounds present in petroleum, *i.e.*, sulfides, disulfides, and thiophenes, do not react with cold, strong sulfuric acid, but are readily dissolved in this reagent. They can be easily regenerated by diluting sulfuric acid or sludge with water.

The treatment of petroleum products with strong sulfuric acid for separation of sulfur compounds may be carried out more selectively if the treatment is performed at low temperatures (about -9 to -12°C 20 - 15°F). Halloran³⁵ showed that the rate of the reaction of hydrocarbons with sulfuric acid at such low temperatures decreases considerably, while the acid retains its activity as a solvent for many sulfur compounds.

In addition to this, Sager⁶⁰ found that the reaction time of sulfuric acid with sulfur compounds is very short, from 4 to 10 seconds at room temperature. After this period of time, equilibrium between the sulfuric acid phase and the gasoline phase is attained, and further treatment does not give any noticeable effect. On the other hand, the reaction between sulfuric acid and unsaturates is much slower; the time required for appreciable removal of the latter is from 30 to 120 seconds at room temperature.

Thus, the selective separation of sulfur compounds by sulfuric acid is quite feasible at low temperatures and short periods of contact between the acid and petroleum product to be treated.

A great deal of analytical work was done with sulfur compounds dissolved in sulfuric acid used for the treatment of gasolines and other products. For instance, McKittrick⁵² diluted an acid sludge formed in the low-temperature treatment of a naphtha, with ice and water. The tar separated was neutralized and steam-distilled; the distillate contained 8 per cent sulfur. It was treated with an equal volume of 95 per cent sulfuric acid at about -10° . A part of the distillate was insoluble in sulfuric acid; this part contained only 0.2 part sulfur. By dilution of sulfuric acid solution only 45 per cent was recovered, neutralized, and distilled. This oil, containing 12.8 per cent sulfur, was solvent-extracted,

fractionated and treated by chemical methods for separation of individual sulfur compounds, as will be seen later.

The sulfur compounds recovered from strong sulfuric acid, particularly in cases in which the action was prolonged and uncontrolled with respect to temperature, cannot be considered as virgin sulfur compounds present in the product treated, at least a part of which were transformed into new compounds by the uncontrolled action of the sulfuric acid.

Separation of Sulfur Compounds with Aluminum Chloride

The extraction of sulfur compounds with aluminum chloride is apparently more selective than with sulfuric acid. The drawback to this method is the same as in the case of sulfuric acid, *i.e.*, the possibility of secondary reactions of many sulfur compounds in the presence of such an active reagent as aluminum chloride.

Polly, Byrns and Bradley⁵⁵ separated sulfur compounds from a California gasoline (0.39 per cent sulfur) with aluminum chloride taken in the proportion of 3½ per cent by weight, corresponding to two moles of aluminum chloride per gram atom of sulfur present. The treatment took place at room temperature for several hours. The fluid sludge layer formed was drawn off and washed with pentane. The sludge then was hydrolyzed by pouring onto chopped ice. The oily phase was separated and freed of pentane. The total extract, containing 17.5 per cent sulfur, was obtained in the amount of 1.6 per cent by weight with respect to the gasoline. The extract was fractionated. More than 70 per cent by volume of the extract was distilled in the original boiling range, the remainder being apparently the polymers and condensation products formed over aluminum chloride.

Tsyganok and Vaniukova⁷⁸ applied the same method for separation of sulfur compounds from a Russian straight-run gasoline rich in sulfur (Ural). From 3 to 9 per cent of aluminum chloride was used. The decomposed "complex" contained up to 10 per cent of sulfur and a comparatively small amount of chlorine (up to 0.67 per cent).

Extraction with Solvents

The extraction of sulfur compounds with solvents, particularly liquid sulfur dioxide, is fairly complete but non-selective. Aromatic hydrocarbons are extracted together with sulfur compounds. As a result, a concentrate of sulfur compounds and aromatic hydrocarbons is obtained. In any case, the concentration of sulfur compounds by solvent extraction is quite feasible. For instance, McKittrick repeatedly extracted them from a Midway cracked gasoline with liquid sulfur dioxide, then with aniline and finally with ethylene glycol acetate. The final extract contained 5.5 per cent of sulfur, compared with 1 per cent in the original gasoline. This concentration was possible at the expense of considerable loss of sulfur compounds in raffinates, so that the final extract contained only 40 per cent of all the sulfur in the original gasoline.

Similar results are obtained in solvent treatment of high-boiling petroleum fractions. The extracts contain a mixture of aromatic hydrocarbons, sulfur compounds, resins, and asphaltenes, which are considered as high molecular weight oxygen-sulfur compounds.

Adsorption of Sulfur Compounds

It would be reasonable to expect that the sulfur compounds in petroleum products could be readily taken up by various adsorbents because of their polar character, compared with hydrocarbons. This is true with respect to the resinous and asphaltic oxygen-sulfur compounds, which are adsorbed effectively and selectively, as will be described later. As far as the low molecular weight sulfur compounds are concerned, such as mercaptans, sulfides, etc., they are adsorbed to a much smaller extent than might be expected from the above standpoint. For instance, it is a well known fact that sulfur compounds are not removed from cracked gasolines by commercial treatment with fuller's earth or other kinds of clay. This is accomplished at high temperatures (400° or higher) by decomposition of the compounds, and is beyond the scope of this volume.

Wood, Sheely, and Trusty⁸⁸ studied the effect of various adsorbents on some sulfur compounds in a naphtha. The concentration of the compounds corresponded to 0.034-0.38 per cent of sulfur. The experiments were carried out by treatment 4 grams of each adsorbent with 50 cc of each stock solution for 1 hour at room temperature. The results are given in Table 129.

Table 129.

Stock Solution	Untreated	% Sulfur in Naphtha Solutions Treated with		
		silica gel	fuller's earth	aluminum oxide
Free sulfur	0.26	0.24	0.25	0.25
Isoamyl mercaptan	0.29	0.09	0.28	0.24
Hydrogen sulfide	0.034	0.03	0.03	0.03
Dimethylsulfate	0.04	0.00	0.00	0.03
Methyl- <i>p</i> -toluenesulfonate	0.15	0.03	0.05	0.15
Carbon disulfide	0.08	0.08	0.08	0.08
<i>n</i> -Butylsulfide	0.30	0.13	0.29	0.30
<i>n</i> -Propyldisulfide	0.38	0.24	0.32	0.36
Thiophene	0.09	0.08	0.08	0.09
Diphenylsulfide	0.05	0.00	0.00	0.05
<i>n</i> -Butylsulfone	0.08	0.00	0.00	0.07

The results indicate that the decreasing order of activity of the adsorbents used is silica gel: fuller's earth: aluminum oxide, the latter being almost completely inactive. The most polar compounds (which are absent in petroleum) *i.e.*, alkyl sulfate, sulfoxide and *n*-butyl sulfone, are completely adsorbed by silica gel. Isoamyl mercaptan, butyl sulfide and propyl disulfide are partially adsorbed by silica gel and almost unaffected by fuller's earth. Thiophene is not affected by any adsorbent in appreciable quantity.

The data of Waterman and van Tussenbroek⁸¹ show that silica gel

readily adsorbs sulfur compounds. Aliphatic and aromatic sulfides, disulfides and mercaptans were investigated. These data in general confirm those of the above authors with the exception of thiophene. According to Waterman and Tussenbroek, thiophene is also partially adsorbed by silica gel, at least at 32-33° for 6 hours. In another article Waterman⁸⁰ gives the following data on successive treatments of a Mexican kerosene (sulfur 1.75 per cent) with 20 per cent by weight of silica gel for two hours:

	Crude	1st Treatment	2nd Treatment	3rd Treatment	4th Treatment
Sulfur content	1.75%	1.37%	1.09%	0.86%	0.65%

Youtz and Perkins⁸⁹ give the following data on the adsorption of various sulfur compounds dissolved in a naphtha (Table 130); 100 cc of each solution were shaken with 20 grams of silica gel for two hours.

Table 130. Adsorption of Various Sulfur Compounds Dissolved in Naphtha by Silica Gel.

Compound	Per Cent of Sulfur— before treatment	after treatment
Ethylsulfide	0.477	0.198
Isoamylsulfide	0.586	0.350
<i>n</i> -Heptylsulfide	0.445	0.104
<i>sec</i> -Heptylsulfide	0.500	0.369
Allylsulfide	0.624	0.335
Phenylsulfide	0.507	0.263
Benzylsulfide	0.400	0.141
Ethylsulfide	0.573	0.365
Isoamylsulfide	0.400	0.250
Trimethylthiophene	0.537	0.413
Trimethylethylthiophene	0.410	0.305
Tetramethylene sulfide	0.430	0.227

Sulfides and disulfides are adsorbed by silica gel approximately with the same ease; thiophenes, however, are adsorbed less readily.

Woodward⁸⁷ was the first to investigate the recovery of the sulfur compounds adsorbed by silica gel from a crude. According to him, the use of superheated steam did not give favorable results. On the contrary, washing of the silica gel after adsorption with naphtha, benzene or ether removed over 90 per cent of the adsorbed material. The remainder was removed by dissolving the gel in sodium hydroxide.

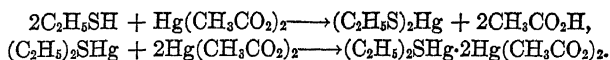
The use of silica gel and some other suitable adsorbents is quite feasible, at least for the partial separation of sulfur compounds. Mercaptans, monosulfides and disulfides are adsorbed much more readily than thiophenes. The adsorbed compounds can easily be recovered by extraction or other methods. The method has been applied to the separation of sulfur compounds in gasolines by Rossini *et al.* (Chapter 4). First, the sulfur compounds and aromatics were separated from the naphthenic-paraffinic portion by adsorption with silica gel. Then, the sulfur compounds were separated from the aromatics by further adsorption. A

much wider application of this method to the separation of sulfur compounds from various fractions may be expected in the near future.

Treatment with Mercury Salts

Organic sulfur derivatives present in oils react with various salts of heavy metals, forming crystalline and non-crystalline compounds, which are insoluble in petroleum oils and thus are separable from the latter. High molecular weight sulfur derivatives may form heavy, thick oils with metallic salts; these oils may become crystalline on standing. The reaction takes place with water, alcohol or acetone solutions of metallic salts. Mercuric salts are chiefly used for these reactions. Various sulfur compounds react in different ways with mercuric salts.

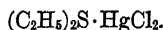
Mercaptans first form mercaptides, which combine with an excess of the mercuric salt, as, for instance, ethyl mercaptan with mercuric acetate gives the following reactions:



According to Birch and Norris,¹⁰ mercuric chloride forms with mercaptans compounds of the same type, but with one molecule of mercuric chloride:

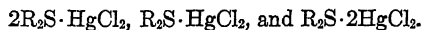


Monoalkylsulfides, including thiophanes, and disulfides combine with mercuric salts directly, as, for instance:

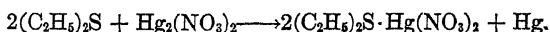


One or more molecules of mercuric chloride may combine with a molecule of the sulfur compound. The double compounds can be recrystallized from alcohol; this is usually accompanied by slight decomposition.

Faragher, Morrell and Comay²⁵ studied the reaction between alkyl sulfides and mercurial salts more thoroughly. The sulfides react with mercuric chloride, forming in general three types of double compounds:



The type depends upon the solvent used, the first type being formed in water, the second in alcohol and the third in benzene. The mercurous salts react with alkyl sulfides in a more complicated manner, precipitating metallic mercury and being transformed into mercuric salts which form the double compounds:

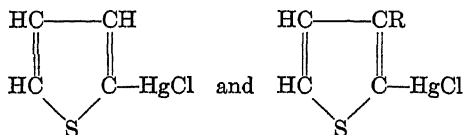


Borgstrom, Bost and McIntire¹³ found that a thiophane (penta-methylene sulfide) dissolved in a naphtha can be removed almost completely by mercuric chloride (2 volumes of naphtha to 1 volume of the saturated mercuric chloride solution).

Faragher, Morrell and Monroe²⁶ found that alkyl sulfides react easily with solid normal mercurous nitrate containing 1 mole of water of hydration. The neutral mercurous nitrate is used in powdered form, as will be described later. Mercurous nitrate reacts also with mercaptans and partially with disulfides. The reaction of mercurous nitrate with disulfides, however, is comparatively slow; thus the separation of sulfides is almost quantitative in the presence of disulfides, if only a short period of contact is used.

Mercurous nitrate reacts with thiophanes as easily as with open-chain aliphatic sulfides, but does not react with aromatic sulfides and thiophenes.⁷ For this reason, mercurous nitrate may be considered as a specific reagent for all aliphatic sulfides and thiophanes.

Thiophenes react with mercuric salts, forming the salts of thiophenes. The reaction is particularly easy with thiophene and β -alkyl derivatives of thiophene. The following compounds are formed in these cases:



These compounds are very stable and can be recrystallized from alcohol without decomposition.

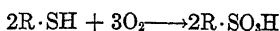
The reaction is performed in alcohol solution in the presence of an excess of mercuric chloride. Hydrogen chloride is formed as a result of the reaction, and therefore sodium acetate is added to bind it.⁷⁰ For instance 295 grams saturated mercuric chloride solution, 60 grams sodium acetate (33 per cent) solution, 525 cc alcohol and 4 grams 2-ethylthiophene are reacted at room temperature. Formation of the precipitate begins in 10-15 minutes, but the reaction is slow and continues for two days. After this, the precipitate is separated by filtration and washed with water. The yield is 81 per cent of theoretical.

When two α -hydrogens of thiophene are alkylated, the reaction is much slower and requires a higher temperature (boiling). The yields of mercury compounds from thiophenes substituted in the α -position are small. Thus the reaction of petroleum distillates with mercury salts does not remove sulfur compounds quantitatively, particularly taking into consideration that derivatives of thiophene are apparently predominant among the sulfur compounds in cracked distillates. Mercuric nitrate reacts with thiophenes in the same manner as mercuric chloride, but the reaction is more complete.

The regeneration of sulfur compounds from their mercurial complexes is usually simple and in many cases quantitative. The complexes can be destroyed by hydrogen sulfide, strong concentrated acids, aqueous ammonia, etc., with regeneration of original sulfur compounds.

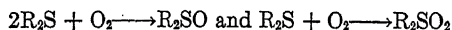
Oxidation and Reduction of Sulfur Compounds

Oxidation is frequently used for identification of sulfur compounds in petroleum. As stated above, the oxidation of mercaptans by mild oxidizers produces disulfides. On oxidation with nitric acid, mercaptans form sulfonic acids which may be compared with known sulfonic acids, at least for low and medium molecular weight paraffins:



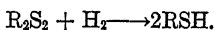
The reaction starts at room temperature and continues on a steam bath until the excess of nitric acid is evaporated. High yields of sulfonic acids are obtained.

Alkyl sulfides yield sulfoxides and sulphones on oxidation with potassium permanganate or hydrogen peroxide:



The alkyl sulfones are crystalline substances known for many alkyl sulfides. The thiophanes form sulfones with particular ease.

Disulphides are easily reduced to mercaptans by hydrogen *in statu nascendi*:



Other sulfur compounds are not reduced under these conditions.

Determination of disulfides by the above reaction may involve losses when volatile mercaptans, such as methylmercaptan, etc., are formed. Agruss and Agruss¹ recommend reducing the disulfides into mercaptans by refluxing the gasoline with zinc dust and glacial acetic acid, collecting any volatile mercaptan formed in a suitable solution, and titrating the mercaptans separately in the latter solution and in the glacial acetic acid.

In addition to the oxidation and reduction reactions, sulfur compounds enter numerous addition reactions due to the reactivity of the sulfur in them. Thus, for instance, alkyl sulfides may react with bromine, methyl iodide, etc. These reactions, however, have so far found no wide application in petroleum chemistry.

Determination of Sulfur Compounds in Gasolines

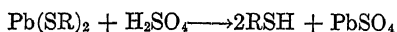
A method of complete analysis of various sulfur compounds in gasolines was developed by Faragher, Morrell and Monroe.²⁸

Hydrogen sulfide is determined by precipitation with an acidified solution of cadmium chloride as cadmium sulfide.

Free sulfur is removed by shaking the sample with metallic mercury. The difference in the total amounts of sulfur (by the lamp method) before and after this procedure gives the percentage of free sulfur.

The mercaptans are determined by one of two methods: (1) The sample, after removal of hydrogen sulfide and sulfur, is shaken with alcoholic solution of sodium plumbite until it is sweet to the doctor test. The lead mercaptides formed are dissolved in alcohol and removed by

separation of the alcohol solution. The amount of mercaptan sulfur is determined by the difference in the total amounts of sulfur (by the lamp method) before and after this procedure. (2) After removal of hydrogen sulfide and sulfur the sample is dissolved in benzene and treated with a suspension of basic lead acetate. The mercaptans react with the lead acetate, forming mercaptides $\text{Pb}(\text{SR})_2$ which dissolve in the benzene. The benzene layer containing mercaptides is separated from the aqueous layer in a separatory funnel. A known quantity of 0.1*N* sulfuric acid is added to the benzene layer in the funnel and the funnel is shaken. The mercaptans are regenerated as a result of this reaction:



The excess sulfuric acid unreacted is determined by titration, and the amount of mercaptans reacted is calculated.

Disulfides are determined in gasoline freed from hydrogen sulfide and sulfur, by reduction to mercaptans with zinc and acetic or sulfuric acid. After reduction the gasoline is treated with alcoholic sodium plumbite to remove the mercaptans formed. A difference in the amounts of sulfur (by the lamp method) before and after this treatment gives the combined mercaptan and disulfide sulfur. The sulfur in disulfides is found by subtracting the mercaptan sulfur previously determined from the combined mercaptan and disulfide sulfur.

The sulfides present in the gasoline after the last removal of mercaptans and disulfides are removed by treatment with powdered mercurous nitrate. The mercurous nitrate forms with sulfides complex compounds insoluble in gasoline. After removal of these compounds, a lamp determination gives the sulfur in the residuum. The sulfide sulfur is calculated by difference. The residual sulfur is that of thiophenes and possibly of some other, unknown sulfur compounds.

Brown¹⁷ modified the Faragher method, particularly with respect to the determination of free sulfur and mercaptans. As stated above, the removal of sulfur by metallic mercury is accompanied by adsorption of mercaptans, resulting in erroneous figures for free sulfur and mercaptans. Brown's procedure is as follows.

The removal of hydrogen sulfide is carried out by treatment with a 10 per cent aqueous solution of sodium bicarbonate for 3 minutes. The treated gasoline is washed, dried, and the total sulfur determined by the lamp method. The content of hydrogen sulfide in terms of sulfur is equal to the difference in the total sulfur content before and after the treatment. Then the free sulfur is removed by treatment with a 3 per cent solution of sodium sulfide at 70° for 10 minutes with a reflux condenser. It has been proved that the sodium sulfide in such a concentration does not affect any other organic sulfur compounds. The free sulfur is determined by the difference in the total sulfur content before and after this procedure. The mercaptan sulfur is determined by treating the gasoline after removal of the free sulfur with a 5 per cent

solution of cadmium acetate. After filtration and washing, the total sulfur is determined by the lamp method, and the mercaptan sulfur is calculated by difference. The alkyl sulfides are removed by shaking 2 or 3 times with a double amount compared to the theoretical amount of solid mercurous nitrate, until the color of the salt remains unchanged. The treated gasoline is filtered, washed, and analyzed for total sulfur. It should be mentioned that up to 10 per cent of disulfides may be involved in the reaction with mercurous nitrate.

The alkyl disulfides are removed by treatment with a 20 per cent solution of sodium sulfide in 80 per cent ethyl alcohol for 4 hours at 60°. After this, the gasoline is separated, washed with water, and treated with a 5 per cent solution of cadmium acetate to remove the mercaptans formed. The total sulfur content is again determined after filtration, washing, and drying.

Another modification of Faragher's method has been recently developed by Ball.⁷ The determination of mercaptan sulfur and hydrogen sulfide is performed by two titrations with silver nitrate, first by titration of the untreated gasoline (total mercaptan sulfur and hydrogen sulfide), and secondly by titration of the gasoline treated with cadmium chloride (mercaptan sulfur). Free sulfur is determined by the butyl mercaptan method, as described above.

The determination of disulfides is made with another portion of the untreated gasoline (150 cc). The gasoline is treated with metallic mercury and then with silver nitrate to remove free sulfur, mercaptans, and hydrogen sulfide. Fifty cc of the gasoline treated in this manner are used for reduction of disulfides to mercaptans by zinc and glacial acetic acid. The mercaptans formed are titrated with silver nitrate, and thus the disulfide sulfur content is calculated.

The remainder of the gasoline that has been treated with mercury and silver nitrate is shaken thoroughly with pulverized mercurous nitrate ($\frac{1}{3}$ by weight) and filtered. This treatment is repeated twice. Aliphatic sulfides, including thiophanes, are separated by this treatment. The difference in the total sulfur content (by the lamp method) before and after this treatment gives the amount of aliphatic sulfide sulfur.

The remainder of the gasoline from the last treatment, *i.e.*, with mercurous nitrate, is shaken thoroughly with pulverized mercuric nitrate ($\frac{1}{3}$ by weight) and filtered. This operation is repeated twice. The difference between the total sulfur content (by the lamp method) before and after this treatment gives the sulfur combined in aromatic sulfides, thiophenes, and disulfides. The aromatic sulfide and thiophene sulfur are calculated by subtracting the value for disulfide sulfur previously found.

After the last treatment the gasoline usually contains some sulfur, which is determined by the lamp method. This, either in the form of some unknown sulfur compounds or not completely separated by the above treatments, is specified as residual sulfur. As will be seen later, in

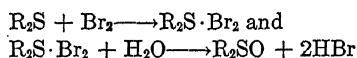
Table 131. Total Content of Sulfur in Various Fractions of Crude Oils.

Fraction	Per Cent of Sulfur
Healdton, Oklahoma, sp. gr. 0.8718 ⁵¹	
Crude oil	0.73
Gasoline	0.09
Naphtha	0.12
Kerosene	0.08
Light gas oil	0.34
Gas oil	0.57
Residuum	1.04
Hull, Texas, sp. gr. 0.8849 (Coke Distillation) ⁵¹	
Crude oil	0.34
Gasoline	0.054
Kerosene	0.075
Gas oil	0.225
Wax distillate	0.381
Heavy distillate	0.610
Coke	1.45
Poza Rica, Mexico, sp. gr. 0.870 ⁵¹	
Crude oil	1.79
Gasoline	0.05
Kerosene	0.12
Gas oil	0.89
Residuum	2.50
Slaughter, W. Texas, sp. gr. 0.869 ^{52a}	
Crude oil	1.92
Gasoline	0.184
Kerosene	0.66
Distillate	1.50
Gas oil	2.09
Residuum	3.34

some cases, for instance, in cracked distillates, the amount of residual sulfur is great, even exceeding the content of sulfur in all other combinations. As has been pointed out by Ball, the results of the analysis in such cases cannot be considered reliable, and the separation of the above classes of sulfur compounds is neither complete nor quantitative.

Other modifications of the analysis of sulfur compounds in gasolines have been discussed by Ball.⁷ Nametkin *et al.*^{53a} suggested a new modification of the method.

Sampey, Slagle and Reid⁶¹ suggested separating sulfides by reaction with bromine and subsequent hydrolysis of the bromine compounds formed:



This method of separation is possible, however, only in the absence of unsaturates, mercaptans and disulfides.

Total Sulfur Content of Crude Oils and Distillates

As stated above, the total amount of various sulfur compounds can be approximately evaluated on the basis of the total percentage of sulfur which, in broad fractions, usually increases with increasing boiling range, as the data of Table 131 clearly show. Thus high molecular weight sulfur compounds predominate in crude oils.

The percentage of sulfur in narrow fractions of gasolines may vary quite irregularly with reference to the boiling range. As a result, sulfur compounds may be concentrated in certain fractions. Morrell and Egloff⁵³ found an uneven distribution of sulfur in broad fractions of California cracked gasolines with maxima and minima. The same phenomenon was observed by Thomas⁷⁵ for a cracked Iran gasoline. Dunn²² gives the following data on the maxima and minima of sulfur content in narrow 1° fractions of a California cracked gasoline (Table 132). The minimum is as low as 0.11 per cent and the maximum as high as 1.58 per cent for a gasoline with a total sulfur content of 0.87 per cent. This phenomenon is sometimes exploited in commercial practice for separation of the most objectionable gasoline fractions which are rich in sulfur; these are treated more severely than the less objectionable fractions.

Table 132. Maxima and Minima of the Sulfur Content in Narrow Fractions of California Cracked Gasoline (0.87 Per Cent Sulfur).

Boiling point of fraction (°F) (50% A.S.T.M. distillation point)	Sulfur content (%)	Boiling point of fraction (°F) (50% A.S.T.M. distillation point)	Sulfur content (%)
35	0.18	132	1.33
52	0.30	143	0.55
63	0.11	156	1.58
71	0.34	166	0.78
88	0.18	178	1.33
103	0.92	188	0.82
118	0.34	198	0.93
		266	0.68

The content of sulfur in a crude oil varies in a wide range from traces to 5 per cent by weight. Accepting the mean molecular weight of crudes as 250 and the presence of one sulfur atom in a molecule, the percentage of sulfur compounds in a crude with 5 per cent of sulfur is calculated as being close to 40 per cent by weight. Thus, the general idea of the predominance of hydrocarbons in crude oils should be accepted with reservation in some cases.

Crude oils rich in sulfur are usually of high specific gravity, *i.e.*, do not contain a large proportion of light distillates, which are low in sulfur. Thus, sulfur is associated mostly with high-boiling fractions and high molecular weight sulfur compounds, *i.e.*, with resins and asphaltenes. The content of the latter predominates over the small content of mercaptans, sulfides, etc., which are present in low-boiling fractions, from gasolines to gas oils inclusive.

The sulfur content of straight-run gasolines is usually low, even for crude oils rich in sulfur. On the contrary, cracked gasolines are much richer in sulfur than straight-run products, evidently because of the decomposition of high molecular weight sulfur compounds into compounds which boil in the range of gasolines.

Usually the sulfur content of cracked gasolines is from 2 to 10 times higher than that of straight-run gasolines from the same crude oil.

Table 133 gives the data on the sulfur content of crude oils, straight-run, and cracked gasolines. It should be pointed out that the values for the sulfur content of straight-run and cracked gasolines depend largely upon the temperature (and time) conditions of the process. This is particularly true of straight-run gasolines, the sulfur content of which may be decreased considerably when moderate temperature conditions of distillation are used.

Table 133. Sulfur Content of Crude Oils and Untreated Straight-run and Cracked Gasolines (400°F E.P.).

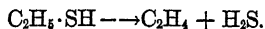
Source	Sp. gr. at 15°	Per cent of sulfur		
		Crude oil	Straight- run	Crack
Oklahoma, Tonkawa	0.815	0.19	0.008	
Oklahoma, Seminole	0.837	0.38	0.015	0.03
Oklahoma, Oklahoma City	0.837	0.20	0.01	0.04
Oklahoma, Healdton	0.872	0.73	0.09	
Texas, East	0.830	0.35	0.012	0.03
Texas, West	0.881	1.55	0.22	0.87
Texas, Panhandle	0.808	0.48	0.085	0.21
Texas, Hull	0.885	0.34	0.054	
Texas, Mirando	0.925	0.20	0.03	0.08
Gulf Coast, Spindletop	0.882	0.18	0.06	0.10
Gulf Coast, Placedo	0.925	0.15	0.03	0.08
Louisiana, Cotton Valley	0.825	0.25	0.03	
Kansas, Ritz	0.840	0.23	0.015	
Kansas, Augusta	0.855	0.29		
Arkansas, Smackover	0.915	2.00	0.04	0.19
Pennsylvania	0.805	0.04	0.005	0.02
Michigan	0.845	0.06	0.02	0.12
Illinois, Salem	0.840	0.25	0.03	0.05
Illinois, Loudon	0.835	0.16	0.02	
Wyoming, Oregon Basin	0.924	3.22	0.28	1.22*
California, Long Beach	0.936	1.15	0.08	
California, Santa Fé Springs	0.845	0.37	0.05	0.2
California, Huntington Beach	0.900	1.30	0.17	0.8
California, Midway	0.935	1.00	0.16	0.45
Canada, Petrolia	0.860	1.00	0.20	
Mexico, Poza Rica	0.871	1.79	0.05	0.8
Mexico, Panuco	0.950	5.2	0.55	1.4
Venezuela, Lagunillas	0.950	2.20	0.07	
Venezuela, La Rosa	0.910	1.80	0.07	0.7
Argentina, Commodore Rivadavia	0.882	0.12	0.04	
Russia, Bibi-Eibat (Baku)	0.865	0.17	0.02	
Russia, Surachany (Baku)	0.870	0.05	0.005	0.015
Russia, New Oilfield (Grozny)	0.840	0.15	0.01	0.02
Iran	0.836	0.8	0.08	0.16
Bahrein Island	0.868	1.80	0.25	
Burma	0.838	0.15	0.03	
Borneo, Miri	0.890	0.4		
Borneo, Tarakan	0.945	0.3		
Iraq	0.844	2.05	0.10	0.34

*End point of this gasoline 507°F

Inorganic Sulfur Compounds

Little can be said on inorganic sulfur compounds or on free sulfur in crude oils. As was stated in Chapter 1, hydrogen sulfide is frequently present in oil-field gases in appreciable amounts, and it is also soluble in

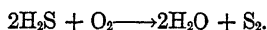
crude oils. In addition to this, hydrogen sulfide is formed on straight-run distillation, and particularly on cracking, as a decomposition product of certain sulfur compounds. For instance, sulfides, disulfides and mercaptans decompose with the formation of hydrogen sulfide. Mercaptans decompose to form olefins and hydrogen sulfide, as, for instance,



This reaction is reversible, so that a mercaptan is formed from an olefin and hydrogen sulfide at lower temperatures. Sulfides and disulfides may form hydrogen sulfide and free sulfur. Thiophenes are more refractory than the derivatives mentioned above.

Such crudes as those of Iraq and some in the Panhandle, which are rich in sulfur, release a large amount of hydrogen sulfide on distillation. The distillation of an Iraq crude in a refinery of Compagnie Francaise resulted in poisoning the vicinity of the refinery. To overcome this difficulty, the crude had to be pretreated and freed of hydrogen sulfide in the oil fields.

Free sulfur is usually absent in virgin crude oils, but is formed very easily when a crude oil or a distillate containing hydrogen sulfide is exposed to air:



As a result of this reaction, elemental sulfur is formed, frequently in well formed crystals in tanks or receivers when the distillates containing hydrogen sulfide are oxidized by air.

Elemental sulfur may be present in cracked products as a result of decomposing mono- and disulfides, as well as of resins and asphaltenes. In freshly distilled straight-run and cracked gasolines the free sulfur is absent because of its high boiling point. The formation of free sulfur in cracked gasolines, however, is usually greater than in straight-run products in view of the higher proportion of hydrogen sulfide in the former. This is usually removed from freshly cracked gasolines by washing with caustic soda to avoid oxidation and formation of free sulfur which, having been formed, cannot be easily eliminated.

The sweetening process, in which a small amount of free sulfur is added, is of course responsible for the presence of sulfur in sweetened gasolines. Table 134 gives a clear idea of the content of free sulfur and sulfur compounds in a gasoline before and after sweetening.³⁷

Carbon disulfide is usually classified as an inorganic sulfur compound; there are no reliable data on its presence in crude oils and gasolines.

Various Organic Sulfur Compounds

Quantitative data on the distribution of various sulfur compounds in crude oils are entirely lacking. There are some meager data on the distribution of these compounds in some straight-run and cracked gasolines obtained by the Faragher method or its modifications (Table 135). These data show that there is an important difference in the distribution

of sulfur compounds in straight-run and cracked gasolines. The former contain mostly mercaptans and sulfides, whereas the latter are rich in the derivatives of thiophene. The observed predominance of thiophenes is apparently a general property of cracked gasolines because the high temperatures used in cracking favor the formation of cyclic structures, which are more stable under cracking conditions.

Table 134. Sulfur Analysis of Gasoline Before and After Sweetening.

	Sulfur in Sour Distillate (% by wt.)	Sulfur in Sweetened Distillate (% by wt.)
Elemental	0.000	0.010
Mercaptan	0.018	0.000
Residual	0.151	0.170
Total	0.169	0.180
Sulfur added	0.016	

Table 135. Sulfur Compounds in Untreated Gasolines.

Sulfur	-Percentage of Sulfur in Gasoline								
	Straight- run Pan- handle ²⁸	Cracked Smack- over ²⁸	Midway cracked ²⁸	Str.- run Oregon Basin ⁷	Cracked Oregon Basin ⁷	Str.- Run Yates ⁸⁵	Reformed Rodessa ⁵⁹	Sura- chany Cracked ²⁰	Str.- run Sterli- tamak ²
Free	0.05	0.00	0.00	0.013	0.000	0.012	0.0000	0.005	0.047
Hydr. sulfide	pres.	pres.	pres.	0.000	0.000	0.003	0.0000	0.01	0.35
Mercaptan	0.04	0.02	0.02	0.003	0.025	0.044	0.0000	0.004	0.25
Disulfide	0.00	0.03	0.11	0.024	0.004	0.032	0.0003	0.006	0.021
Sulfide (aliphatic)	0.00	0.00	0.02	0.159	0.008	0.082	0.0009	0.003	0.17
Thiophene and aromatic	{0.00	0.15	0.95	0.000	0.416	0.049	{0.0021	0.038	0.00
Residual				0.018	0.727				0.085

The mercaptan content of straight-run and cracked gasolines was studied by many investigators because of its practical importance in the sweetening process. Table 136 gives classified data on the content of mercaptan sulfur in various gasolines.

Ball has given the following data on the content of various sulfur compounds in straight-run Oregon Basin kerosene distillate:

Hydrogen sulfide	0.000 per cent
Free sulfur	0.000
Mercaptan	0.000
Disulfide	0.003
Aliphatic sulfide	0.313
Arom. sulfide and thiophene	0.289
Residual sulfur	0.213

According to Velikovsky,⁷⁹ the content of sulfur compounds in straight-run Sterlitamak (Ural) kerosene, rich in sulfur, is as follows:

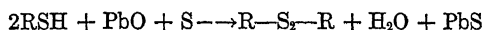
Hydrogen sulfide	0.048 per cent
Free sulfur	0.062
Mercaptan	0.184
Disulfide	0.16
Aliphatic sulfide	0.26
Thiophene	0.00
Residual sulfur	0.018

All these figures are given in the terms of combined sulfur in the compounds specified. The data for kerosenes should be considered as approximate in view of the difficulties connected with the analytical procedures for high-boiling fractions, discussed above.

Table 136. Total and Mercaptan Sulfur in Various Gasolines (400°F E.P.).

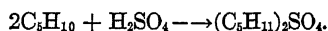
Gasoline	Per Cent of Sulfur	
	Total	Mercaptan
Pennsylvania, straight-run	0.005	0.001
Pennsylvania, cracked	0.02	
Mid Continent, straight-run	0.010	0.004
Mid Continent, cracked	0.040	0.009
East Texas, straight-run	0.012	
East Texas, cracked	0.035	0.012
West Texas, straight-run	0.22	0.075
West Texas, cracked	0.65	0.14
Texas Panhandle, straight-run	0.09	0.04
Illinois, straight-run	0.040	0.015
Illinois, cracked	0.10	0.03
Michigan, straight-run	0.02	
Michigan, cracked	0.12	0.05
Arkansas Smackover, straight-run	0.04	
Arkansas Smackover, cracked	0.20	0.02
California, straight-run	0.175	0.050
California, cracked	0.355	0.055

Little can be said of the presence of polysulfides, sulfonic acids, and esters of sulfuric acid in some refined oil products. Such compounds, even in small quantities, are highly undesirable and are due to certain shortcomings in the refining process. Polysulfides may be produced in the so-called doctor sweetening treatment of gasolines, in which litharge and free sulfur are employed for transformation of mercaptans into disulfides:



In the presence of an excess of free sulfur polysulfides can be formed. They may be present in conventionally sweetened gasolines in minute amounts not exceeding 0.001 per cent.

Esters of sulfuric acid may be formed as a result of heavy and uncontrolled treatment of cracked gasolines with sulfuric acid, involving the reaction with olefins,²¹ as, for instance:



The neutral esters formed are soluble in the treated gasoline and can be partially distilled in rerunning with the gasoline.

Sulfonic acids in the form of soaps may be present in kerosenes or lubricating oils treated with sulfuric acid. This treatment converts the aromatic hydrocarbons present in kerosene or lubricating stocks into sulfonic acids which are partially soluble in the oils treated (Chapter 3). Neutralization of the oil with sodium hydroxide solution produces soaps of sulfonic acids, which are also soluble in oils. An insufficient washing of the neutralized oils results in the presence of sulfonates in the finished products.

Individual Sulfur Compounds

Our knowledge of the individual sulfur compounds in crude oils and distillates is very meager. While high molecular weight oxygen-sulfur

derivatives (resins and asphaltenes) undoubtedly preexist in crude oils, very little is known of the origin of low and medium molecular weight sulfur derivatives, such as mercaptans, sulfides, etc., which occur in distillates. It is quite possible that at least a portion of such compounds is formed on distillation of crude oils at the expense of some unknown unstable virgin sulfur compounds. According to Mabery and Smith,⁴⁸ the organic sulfides preexist in crude oil. They distilled a crude oil under diminished pressure and extracted sulfur compounds from distillates with sulfuric acid or with mercuric chloride. The compounds separated from the acid sludge or from the mercuric chloride double compounds were identical with the compounds obtained from commercial distillates and sludges. On the other hand, disulfides detected by Birch and Norris¹⁰ in Iranian straight-run gasolines are thought to be a result of the oxidation of mercaptans present in the gasolines.

Partial decomposition of the sulfur compounds in crude oils takes place even in straight-run distillation. Bjerregaard¹¹ showed that the distillates and residuum produced in straight-run distillation contain less sulfur than the virgin crude. The loss in sulfur after distillation was in some cases as high as 30 per cent of the total.

Thorne and Murphy⁷⁷ found that, on coke distillation, Wyoming black crudes rich in sulfur produce hydrogen sulfide and coke, containing from 51.6 to 88.0 per cent of the total sulfur in the oil. Thus, a great part of original sulfur compounds is converted into some newly formed decomposition and condensation compounds.

As far as the sulfur compounds of cracked gasolines and other distillates are concerned, it is quite certain that those present in such distillates are formed as a result of decomposition of high molecular weight sulfur or oxygen-sulfur compounds.

Various mercaptans have been isolated from straight-run gasolines. Methyl and ethyl mercaptans (b.p. 6° and 36° respectively) are usually present in field and cracked gases containing hydrogen sulfide, and in gasolines produced from such gases. The content of methyl and ethyl mercaptans may be as high as 0.5 to 1.0 per cent in some gases high in sulfur.

Birch and Norris¹⁰ investigated a straight-run gasoline of Maidan-i-Naphtun crude oil and isolated a series of mercaptans from light fractions by extraction with caustic soda solution and by subsequent fractionation of the mercaptans. The latter were identified by double compounds with HgCl_2 , by oxidation to sulfonic acids, etc. The following mercaptans were separated:

Ethyl mercaptan
Isopropyl mercaptan in fraction 56°-58°
Isobutyl mercaptan in fraction 86°-88°
Isoamyl mercaptan in fraction 116°-118°

Williams and Richter⁸³ also separated ethyl mercaptan from a cracked West Texas gasoline. The mercaptan was obtained from the

"acids" extracted from the gasoline by sodium hydroxide solution. The mercaptan boiled at 35°-37° and was converted into C_2H_5SAg for identification. Wiezevich, Turner and Frolich⁵² give the following data on the composition of mercaptans extracted from gasolines in a refinery:

Methyl mercaptan	30%	C. W.
Ethyl mercaptan	53	" "
Propyl mercaptan and higher	17	" "

As should be expected, the caustic treatment produces low molecular weight mercaptans; the heavier ones are little affected by this treatment.

Happel, Cauley and Kelly³⁸ give the following typical distribution of various mercaptans in straight-run and cracked Mid-Continent gasolines:

Mercaptan	Per cent of total mercaptan content in	
	Straight-run	Cracked
Methyl	4	19
Ethyl	6	34
Propyl	13	18
Butyl	19	15
Amyl	18	9
Hexyl +	40	5
	<hr/> 100	<hr/> 100
Total mercaptan sulfur	0.0265	0.0357

Thus, straight-run gasolines have a larger percentage of heavier mercaptans than cracked gasolines which contain predominantly C_1 to C_4 mercaptans, apparently because of the effect of cracking.

Windle^{35a} found that a substantial part of the mercaptans in Bahrein cracked gasoline (total sulfur 0.12% and mercaptan sulfur 0.025%) consists of thiophenol.

Mabery and Smith⁴⁶ investigated the sulfides present in a kerosene distillate from an Ohio (Lima) crude oil, which contained 0.5 per cent sulfur. The sulfur compounds were obtained from the acid sludge that had been produced on refining the burning oil. The oil obtained contained 14.97 per cent sulfur. Repeated fractionation of this oil under 150 mm pressure gave narrow fractions which were treated with mercuric chloride. The double compounds produced corresponded closely to mercuric compounds $(CH_3)_2S \cdot HgCl_2$ and $(C_2H_5)_2S \cdot HgCl_2$, whereas the higher fractions gave probably mixtures of $(C_3H_7)_2S \cdot HgCl_2$ and $(C_4H_9)_2S \cdot HgCl_2$.

Another investigation was made with the naphtha from Findley crude oil. The naphtha was treated with aqueous mercuric chloride and the precipitate formed was filtered, dried, and decomposed by hydrogen sulfide in alcohol solution. After filtration, the alcohol solution was diluted with water, and the oil formed was separated, washed, dried, and subjected to fractional distillation. The following sulfides were thought to be identified:

Dimethylsulfide
Diethylsulfide (boiling range 88°-92°)
Ethylpropylsulfide (boiling range 110°-112°)
Dipropylsulfide (in fraction 115°-125°).

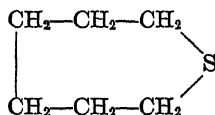
High-boiling sulfides were obtained from the acid sludge by the method described above. The double mercuric compounds were decomposed with H_2S , and the sulfides liberated were analyzed. The following were supposed to be identified:

Ethylpentylsulfide (boiling range $95^\circ\text{--}100^\circ$, 100 mm)
 Diisobutylsulfide (boiling range $110^\circ\text{--}115^\circ$, 100 mm)
 Di-*n*-butylsulfide (boiling range $117^\circ\text{--}125^\circ$, 100 mm)
 Butylpentylsulfide (boiling range $135^\circ\text{--}140^\circ$, 100 mm)
 Dipentylsulfide (boiling range $150^\circ\text{--}155^\circ$, 100 mm)
 Dihexylsulfide (boiling range $100^\circ\text{--}170^\circ$, 100 mm)

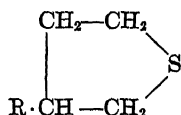
Mabery and Quayle⁴⁵ studied a Canadian crude oil. The distillates were treated with mercuric chloride and the double compounds formed were decomposed with H_2S as in the previous investigation. The fractionation of the sulfur compounds was believed to produce the following sulfides:

Hexylthiophane, $\text{C}_6\text{H}_{12}\text{S}$ (b.r. $125^\circ\text{--}130^\circ$)
 Heptylthiophane, $\text{C}_7\text{H}_{14}\text{S}$ (b.r. $158^\circ\text{--}160^\circ$)
 Octylthiophane, $\text{C}_8\text{H}_{16}\text{S}$ (b.r. $167^\circ\text{--}169^\circ$)
 Isooctylthiophane, $\text{C}_8\text{H}_{16}\text{S}$ (b.r. $94^\circ\text{--}96^\circ$, 50 mm)
 Nonylthiophane, $\text{C}_9\text{H}_{18}\text{S}$ (b.r. $193^\circ\text{--}195^\circ$)
 Decylthiophane, $\text{C}_{10}\text{H}_{20}\text{S}$ (b.r. $201^\circ\text{--}209^\circ$)
 Undecylthiophane, $\text{C}_{11}\text{H}_{22}\text{S}$ (b.r. $128^\circ\text{--}130^\circ$, 50 mm)
 Decylthiophane, $\text{C}_{10}\text{H}_{20}\text{S}$ (b.r. $201^\circ\text{--}209^\circ$)
 Quatdecylthiophane, $\text{C}_{14}\text{H}_{28}\text{S}$ (b.r. $266^\circ\text{--}268^\circ$, 750 mm)
 Sexdecylthiophane, $\text{C}_{16}\text{H}_{32}\text{S}$ (b.r. $283^\circ\text{--}285^\circ$, 750 mm)
 Octadecylthiophane, $\text{C}_{18}\text{H}_{36}\text{S}$ (b.r. $290^\circ\text{--}295^\circ$)

The authors found that sulfides separated from Canadian crudes differ substantially from those from Ohio crudes, the latter being similar to synthetic aliphatic sulfides. Sulfides from Canadian crudes are oxidized much more easily than aliphatic sulfides, producing sulfones, as, for instance, $\text{C}_6\text{H}_{12}\text{S} \rightarrow \text{C}_6\text{H}_{12}\text{SO}_2$. The authors believed that the sulfides from Canadian crudes have a cyclic structure, being either sulfurized polymethylenes of the general formula:



or alkyl derivatives of sulfurized cyclobutane, cyclopentane or cyclohexane rings, as, for instance,



Thierry⁷³ diluted with water and extracted with chloroform the acid sludge from the treatment of light distillates from an Iranian crude oil.

The following compounds are thought to be isolated by fractionation:

Methylethylsulfide (b.r. 68°-70°)
Methylpropylsulfide (b.r. 89°-92°)
Butylthiophane (b.r. 120°-121°)
Pentylthiophane (b.r. 138.5°)

The compounds were identified by the double compounds with mercuric salts and by oxidation to sulfones. The thiophanes isolated corresponded to those synthesized by Grischkevitch-Trochimovsky³⁴ and von Braun and Strumpler.¹⁶

Teutsch⁷² studied the sulfur compounds of a Panuco crude oil and found that these compounds are of cyclic structure and similar to the thiophanes of Mabery. A light distillate of the Panuco crude oil, containing 0.79 per cent of sulfur, was fractionated into 5° fractions boiling from 70° to 170° at atmospheric pressure and from 95° to 135° at 46 mm. The sulfur content of these fractions increases gradually; in the fraction boiling up to 100° it is low (less than 0.1 per cent), due to the relatively small proportion of mercaptans and alkyl-sulfides in the crude. Higher fractions contain from 0.0124 to 1.03 per cent of sulfur. The low-boiling fractions up to 143° were treated with mercuric chloride, and the double compounds formed were recrystallized from alcohol. The elemental composition and melting points of some double compounds, compared with those of Grischkevitch-Trochimovsky, allowed identification of tetrahydro-thiophene and methyl-tetrahydrothiophene as constituents of the fractions 105°-110° and 110°-125°. In other fractions some other cyclic sulfides of unknown structure were separated. High-boiling fractions (above 143°) of sulfur compounds were obtained from sulfuric acid sludge by fractionating its oily constituents. Two cyclic sulfides of unknown structure were separated from the fractions. The following cyclic sulfides or thiophanes were separated and identified:

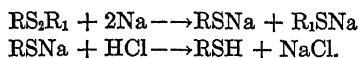
Butylthiophane (tetrahydrothiophene) in fraction 105°-110°
Pentylthiophane (α -methyltetrahydrothiophene) in fraction 120°-125°
Pentylthiophane (pentamethylenesulfide) in fraction 120°-130°
Hexylthiophane in fraction 140°-143°
Octylthiophane
Octylthiophane (isomer) } in acid sludge

Friedman and Canseso²⁹ confirmed Teusch's results for Panuco straight-run gasoline. The identification of tetrahydrothiophene, α -methyltetrahydrothiophene and pentamethylenesulfide should be considered satisfactory in view of the identity of the double compound with mercuric chloride with those obtained by Grischkevitch-Trochimovsky from synthetic tetrahydrothiophene and its derivatives.

According to Polly, Byrns and Bradley,⁵⁵ California straight-run gasolines are also rich in thiophanes. These authors identified in such a gasoline (Santa Maria Valley) tetramethylene sulfide, 2- and 3-methyl tetramethylene sulfide and probably some other alkyl tetramethylene sulfides. No individual disulfides were isolated from straight-run or cracked gasolines.

The formation of disulfides as a result of the oxidation of mercaptans in straight-run and cracked distillates is unquestionable, but it is probable that they are also present in virgin non-oxidized cracked distillates. It should also be remembered that in commercial sweetened gasolines at least a part of the disulfide content is due to sweetening (page 369).

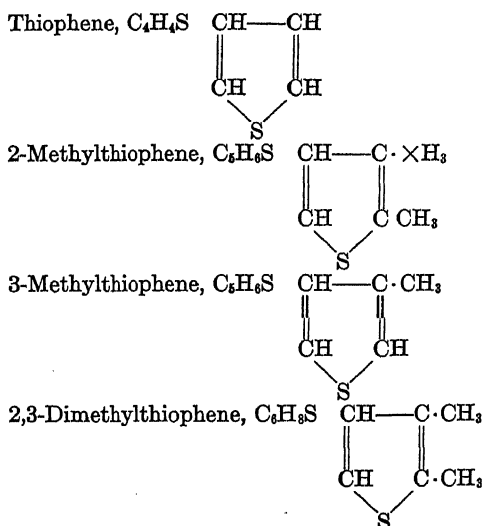
An indirect hint as to the presence of disulfides in high-boiling distillates was given by Ferrer.²⁷ He desulfurized a treated Pennsylvania oil (sulfur content 0.32 per cent) with metallic sodium and decomposed with weak hydrochloric acid the sulfur compounds formed. The decomposition products contained amyl, heptyl and octyl mercaptans. The author believes that these mercaptans are formed as a result of the reaction of original disulfides with sodium:

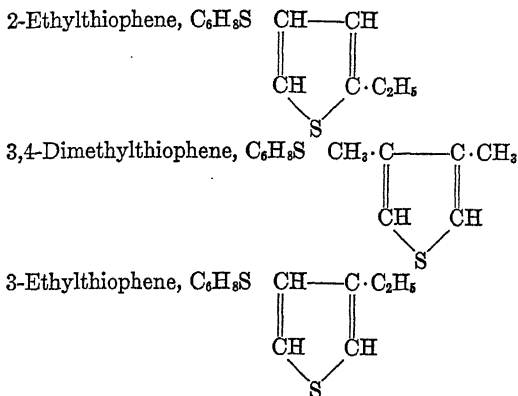


There are some doubtful data on the presence of thiophene in crude oils and straight-run distillates. Only in cracked gasolines were thiophene and its derivatives positively identified.

McKittrick⁵² concentrated the sulfur compounds of a cracked California gasoline by extraction, as described above. The final extract, containing 5.5 per cent of sulfur, was carefully fractionated. The fractions rich in sulfur were treated with mercuric chloride. The extract contained mostly the derivatives of thiophene, which apparently predominate in cracked gasolines. This finding is in agreement with the analytic data on the distribution of sulfur compounds in cracked gasolines, discussed above.

The following thiophenes were identified by this author by physical properties and by the mercuric double salts formed:





It should be pointed out that the identification of many sulfur compounds listed above is doubtful. For instance, the individual sulfides of Mabery were identified only on the basis of boiling temperatures, usually in a comparatively wide boiling range, and of ultimate analysis. Notwithstanding this, the general conclusions of Mabery on the presence of two series of sulfides in oils, alkylsulfides and cyclic sulfides, or thiophanes, were well supported by later investigators. The presence of the latter was not proved by Mabery, since such compounds were unknown at that time. Later, Thierry and Teutsch identified some thiophanes separated from Iranian and Panuco crude oils as tetrahydro-thiophenes and pentamethylenesulfide, which were synthesized by Grischkevitch-Trochimovsky. The identification of the thiophene derivatives by McKittrick is also reliable.

The knowledge of organic sulfur compounds is so far much behind that of hydrocarbons or even oxygen compounds. Quantitative data on the presence of individual sulfur compounds are entirely lacking; those identified were obtained from a very limited number of crudes (Ohio, Canada, California, Panuco) and from low-boiling fractions. The sulfur compounds, even the classes present in medium- and high-boiling fractions, remain unknown.

Nitrogen Compounds

The nature of nitrogen compounds in crude oils is entirely obscure. According to some earlier qualitative data, organic nitrogen bases can be extracted directly from certain crudes. Pott *et al.*⁵⁶ found, however, that California crudes yield practically no bases on acid extraction, whereas distillates from these crudes contain a considerable amount. The nitrogen bases in distillates appear to result from decomposition of some neutral complex nitrogen compounds at distillation temperatures.

As will be seen later, at least some of the nitrogen is combined in resinous compounds extracted by solvents from high-boiling fractions. These may contain sulfur and oxygen also.

The nitrogen compounds in crude oils undoubtedly originated from the organic material which was the mother-substance of petroleum. The minute amount of such compounds in crude oils is due to the fact that the greater part of the organic nitrogen was decomposed to nitrogen and ammonia.

Table 137. Total Content of Nitrogen in Crude Oils.

Origin	Specific Gravity	Per Cent of Nitrogen
Titusville, Pa.	0.7904	0.018
Emblenton, Pa.	0.8809	0.0136
" "	0.8007	0.012
Dudley, Ohio	0.8238	0.027
Malto, Ohio	0.8326	0.039
Corning, Ohio	0.8404	0.041
Marietta, Ohio	0.7907	0.016
Newport, Ohio	0.7904	0.024
Mecca, Ohio	0.9023	0.054
Cabin Creek, W. Virginia	0.8139	0.029
Bartlesville, Okla.	0.8625	0.074
Humble Field, Texas	0.9066	0.058
" " "	0.8227	0.015
Sour Lake, Texas	0.9302	0.067
Beaumont, Texas	0.9175	0.023
Morris, Kansas	0.8499	0.035
Jennings, La.	0.9054	0.048
Caddo, La.	0.8584	0.050
Vinton, La.	0.9014	0.067
Ventura, California		0.381-0.448
Midway, California		0.426
Coalinga, California		0.358
Ojai Lease, California		0.802
St. Fé Springs, California		0.254
Mexican, heavy		0.358
Mexican, light		0.326
Trinidad, light		0.1-0.2
Colombia		0.226
Venezuela		0.231
Baku, Russia	0.865	0.071

Two methods of determining the total content of nitrogen in crude oils or distillates are available: the Dumas combustion and the Kjeldahl methods. The Dumas method gives quite reliable results for oils in which the total nitrogen content is not too small. In most cases, however, the Kjeldahl method is preferable, notwithstanding an earlier criticism of this technique as applied to crude oils.

Mabery⁴⁴ pointed out that the combustion method requires special precautions on account of the minute percentage of nitrogen in crude oils. Any traces of nitrogen must be removed from sodium bicarbonate and carbon dioxide as well as from the copper oxide used for combustion.

Pott, Armstrong, Cogburn and Bailey⁵⁸ developed the following modification of the Kjeldahl method for determining the total nitrogen content in oils, and showed that this method gives results which are practically identical with those obtained by the combustion method by Mabery.⁴⁴ Procedure: One to 5 grams of the sample are digested with 150 cc of sul-

furic acid, 50 grams of potassium sulfate, 2.5 grams of mercuric oxide, and 2.5 grams of copper sulfate. Depending on the nature and weight of the oil, the digestion continues from 30 minutes to 2 hours to obtain a clear, dark green color. The remaining procedure is conventional.

Table 137 includes the most reliable data on the total content of nitrogen in crude oils. The earlier data of Mabery, giving a high percentage of nitrogen in California crudes (from 1.5 to 2.5 per cent) appear to be erroneous and are not included into the table. According to Pott *et al.*, the maximum nitrogen content found in any crude oil does not exceed 0.815 per cent.

There is a certain parallelism between the percentage of sulfur and nitrogen: crude oils rich in sulfur are usually rich in nitrogen, and *vice versa*. This relationship is apparently related to the organic origin of crude oils, the sulfur and nitrogen compounds of which are a result of the transformation of proteins. On the other hand, this relationship cannot be too close, since the formation of certain sulfur compounds in crude oils is quite possible as a result of secondary reactions of the oils with sulfates *in situ* (page 350). The total nitrogen content in most American and other crudes is very small, not exceeding a few hundredths of one per cent. California and some Mexican oils are rich in nitrogen, the content of which amounts to 0.5 per cent.

No methods of separating nitrogen compounds directly from crude oils have been developed. Solvent extraction concentrates the nitrogen compounds in the extracts with oxygen and sulfur compounds as well as with aromatic hydrocarbons. Gilpin and Schneeberger²⁸ showed that nitrogen compounds are adsorbed by fuller's earth. The effect of the adsorption, however, was not very conspicuous, and the last fraction retained by the adsorbent—the richest in nitrogen—contained 0.94 per cent of nitrogen as compared with 0.761 per cent in the crude oil. This method, nevertheless, may be of use to concentrate the virgin nitrogen compounds in crude oils. As will be seen later, the distillates contain nitrogen organic bases, which are apparently formed during distillation. Only these nitrogen organic bases have been separated and investigated up to the present time.

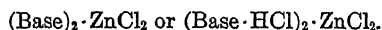
Methods of Separating Nitrogen Bases

The methods in question were developed by Bailey and his co-workers. The separation of nitrogen bases from distillates can be performed by dilute sulfuric acid. It is more practical, however, to concentrate the bases by solvent extraction, *i.e.*, by liquid sulfur dioxide, which extracts nitrogen bases as well as aromatic hydrocarbons and oxygen and sulfur compounds. The extract containing the bases is treated with dilute sulfuric acid, and treatment of the solution with sodium hydroxide then liberates free nitrogen bases.

Mair, Willingham, and Streiff⁴⁹ showed that nitrogen compounds are extracted by sulfur dioxide more selectively than oxygen or sulfur com-

pounds. As a result, the nitrogen compounds are concentrated chiefly in the first 10 per cent extracted. The total extract of a Mid-Continental lubricating stock contained 0.1 per cent nitrogen, 0.9 per cent sulfur and 0.5 per cent oxygen. The free nitrogen bases are carefully separated into narrow fractions which are further investigated by various chemical methods. Usually fractionation alone does not produce pure bases.

The nitrogen bases readily form various salts and double compounds, as, for instance, with platinic chloride, mercuric chloride, sulfur dioxide, etc. Thus the narrow fractions of nitrogen bases can be transformed into crystalline salts which are separated and purified by fractional crystallization. The picrates are frequently used for this purpose. Some of them, which are difficultly soluble in cold acetic acid or alcohol, are recrystallized from these solvents. The crystalline double compounds with platinic, zinc or mercuric chloride are also used for separation and purification of nitrogen bases. For instance, Mahan and Bailey⁴⁸ suggested the use of zinc chloride for purification of nitrogen bases from water, hydrocarbons, sulfur and phenolic compounds. The bases give double compounds of the type:



The double compounds are formed as precipitates which can be decomposed at higher temperatures, with regeneration of free base or base hydrochloride.

Bailey showed that the nitrogen bases in oil distillates may be of two types: aromatic and non-aromatic. Perrin and Bailey⁵⁴ separated these types by the method of "cumulative extraction." The mixture of bases is transformed into chlorides by dissolving it in an excess of dilute hydrochloric acid. The chlorides formed differ in their solubility in organic solvents, such as chloroform, depending on their chemical nature. The chlorides of non-aromatic bases are much more soluble in the solvents used than are those of aromatic bases. As a result, repeated treatment of the chlorides in aqueous solution with chloroform extracts chiefly non-aromatic bases, the aromatic bases remaining in the acid aqueous solution. By this method the absence of non-aromatic bases in a cracked naphtha was proved.

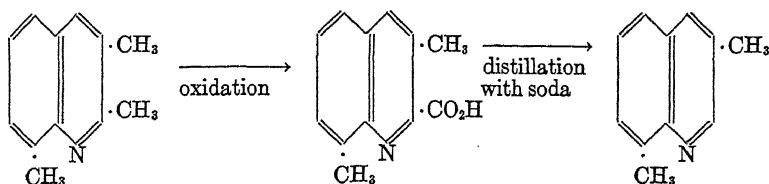
It should be pointed out, however, that at least some of the "non-aromatic" base chlorides extracted by chloroform may actually be the chlorides of highly alkylated aromatic bases, which lose to a certain extent their aromatic properties because of the accumulation of paraffinic side chains.

Another method for separating aromatic and other bases is by fractional "degassing" of acid sulfites (Roberts and Bailey⁵⁸). The nitrogen bases are saturated with sulfur dioxide, and the insoluble salts formed are fractionally "degassed" or destroyed:



The decomposition is effected first at 20° by passing air. The most unstable salts of the bases of unknown composition are decomposed at this temperature. The following fractions are decomposed at 50° and then at 80°. The aromatic bases form the most stable salts, which are concentrated in the undecomposed residuum.

As will be seen later, many organic bases isolated by Bailey are polymethylated derivatives of quinoline, isoquinoline and pyridine. Oxidation of such an organic base by chromic or permanganic acid may produce a monocarboxylic acid of known structure. This carboxylic acid, on distillation with soda lime, gives off carbon dioxide and produces a degraded methyl derivative, *i.e.*, one having fewer methyl groups. For instance, Pott *et al.*⁵⁶ described the following procedure for the identification of 2,3,8-trimethylquinoline separated from a California kerosene:



An improved modification of the oxidation method has been described by Glenn and Bailey. A ketone group in the side chain is formed under certain conditions instead of the carboxylic group, or a mixture of both compounds—an acid and a ketone. The formaldehyde compounds discussed below may also be oxidized, with formation of the same oxidation products.

Other reagents used for oxidation of nitrogen bases are selenium dioxide⁶⁸ and ozone.⁶⁹

Mabery and Wesson⁴⁷ oxidized nitrogen bases with potassium permanganate at boiling temperature, gradually adding potassium permanganate until the color of the solution disappeared very slowly. The oxidation lasted from 2 to 3 days; from 24 to 40 grams of potassium permanganate was consumed by 3 grams of the base. Under these conditions, polycarboxylic acids apparently were formed.

Hydrogenation is another method of investigating the structure of nitrogen bases. The negative result of hydrogenation may be a proof of the non-aromatic structure, provided the most efficient methods are applied. It should be kept in mind that some alkylated nitrogen bases can be hydrogenated only with difficulty. The base $C_{16}H_{25}N$, separated by Bailey and his associates, was thought to be non-aromatic, but hydrogenation was accomplished at high pressure and at 250° over Raney nickel. The consumption of hydrogen was 6 hydrogen atoms per molecule. The dehydrogenation yielded the original base. As the base has two rings, the hydrogenation proved that one of them is aromatic.

The reaction of nitrogen bases with methyl iodide, leading to the formation of a quaternary ammonium salt may also give some important

conclusions. For instance, a trimethyl quinoline separated from a California kerosene did not react with methyl iodide. It was concluded therefrom that there is a methyl group in positions 2 and 8, which hinders the activity of the nitrogen atom (steric hindrance).

The condensation of methylquinolines of unknown structure with formaldehyde or phthalic anhydride may also give some clues. It is known that the methyl group at position 2 is particularly active, reacting with one molecule of phthalic anhydride, forming phthalones, or with three molecules of formaldehyde, forming solid condensation products. The reaction with phthalic anhydride takes place at 200°, and the phthalone formed is crystallized from organic solvents in well formed crystals.

In many cases the identity of the quinoline derivatives was substantiated by comparison with synthetic compounds produced by conventional synthetic methods.

Nitrogen Compounds Identified in Petroleum

Our knowledge of individual nitrogen compounds in petroleum is limited to nitrogen bases which have been separated from naphthas, kerosenes, and to some extent from light gas oils.

The distillates contain non-basic nitrogen compounds, in addition to bases. According to Pott *et al.*,⁵⁷ the kerosene distillate from McKittick crude oil (California), with a total nitrogen content of 0.055 per cent, contains approximately 55 per cent of basic nitrogen compounds which are extractable with dilute sulfuric acid. In the high-boiling distillates, with the greater total nitrogen content, the proportion of basic to non-basic nitrogen compounds is smaller, decreasing with increasing distillation temperature.

Practically nothing is known of the chemical nature of the nonbasic nitrogen constituents. The authors cited postulate that these compounds may be of the pyrrole, indole and carbazole types, or of a more complex heterocyclic structure containing both nitrogen and sulfur. The last suggestion may include such compounds as resins or asphaltenes containing oxygen and sulfur, which are considered as elemental constituents of resins and asphaltic compounds. Mair, Willingham and Streiff⁴⁹ found, however, that the extraction of nitrogen compounds from a lubricating stock takes place almost quantitatively in the first 10 per cent extracted, whereas oxygen and sulfur compounds are extracted more gradually, and are present in all fractions extracted.

This very interesting observation shows that nitrogen is not necessarily combined with high molecular weight sulfur and oxygen compounds or, at least, with all such compounds which may be present in high-boiling fractions. It is possible that the nitrogen compounds extracted in the first portion also include oxygen and sulfur.

The nitrogen bases in cracked products are simpler and less numerous than in straight-run products. Bratton and Bailey¹⁵ investigated the nitrogen bases in a cracked gasoline (b.r. 36°-171°) obtained in cracking

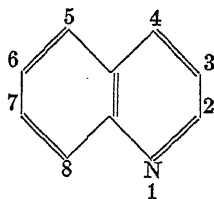
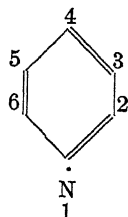
a California gas oil and residuum (454°, 54-58 atm). The crude bases (b.p. 115°-240°) were extracted from this gasoline in the quantity of 0.004 per cent by volume. Non-aromatic nitrogen bases were entirely absent. Nine aromatic nitrogen bases—quinoline, quinaldine and seven pyridine homologs—were isolated (Table 138). The separation and isolation of these bases was performed by amplified distillation (page 65) and by crystallization of picrates and double mercuric chloride salts. It is not believed that any other nitrogen bases, present beyond a negligible amount, were overlooked.

The variety of nitrogen bases in cracked gasolines is much less than in straight-run distillates due, obviously, to cracking. The non-aromatic bases, unstable under cracking conditions, either decompose or produce more stable aromatic types. Quinoline and quinaldine were not detected in straight-run gasolines and kerosenes, and appear to be the products of dealkylating more complex alkylated quinolines, which are present in straight-run distillates.

Egushi²⁴ isolated a series of pyridine homologs from a shale oil, proving that these homologs occur in the decomposition products of crude oils, shales, and coal.

Table 138. Nitrogen Bases Separated from California Cracked Naphtha.

2-methylpyridine
4-methylpyridine
2,4-dimethylpyridine
2,5-dimethylpyridine
2,6-dimethylpyridine
3,5-dimethylpyridine
2,4,6-trimethylpyridine
Quinoline
2-methylquinoline (chinaldine)



Pyridine homologs are almost absent in straight-run gasolines, which do not contain an appreciable quantity of nitrogen compounds.

California straight-run kerosene distillates and to some extent gas oils were thoroughly investigated by Bailey and his co-workers as a source of nitrogen bases. Both non-aromatic and aromatic nitrogen bases occur in these distillates, the first ones predominating. The ratio of the non-aromatic to the aromatic bases is close to 85:15 in California kerosene distillates.

The aromatic nitrogen bases in kerosene distillates belong to the derivatives of quinoline. Table 139 includes all the nitrogen aromatic bases,

which have been separated from California kerosene distillates. It is of interest that neither quinoline itself nor its monomethylated derivatives have been detected in straight-run kerosenes. Thus straight-run distillates contain mostly polymethylated or, in general, polyalkylated derivatives of quinoline. The alkyl quinolines boiling in the range of kerosenes may have up to four methyl groups, or two or three methyl groups with a higher group, from ethyl to butyl. Cracked products contain quinoline and monomethylquinolines at the expense of polyalkylated or highly alkylated derivatives, which are present in straight-run products and are dealkylated on cracking.

Table 139. Nitrogen Bases Separated from California Straight-run Distillates.

Base	Boiling Range (°C)	Ref.
2,3-Dimethylquinoline	263-267	9
2,4-Dimethylquinoline	" "	"
2,8-Dimethylquinoline	253-256	41, 4
2,3,8-Trimethylquinoline	276-277	57
2,4,8-Trimethylquinoline	273	54
2,3,4,8-Tetramethylquinoline	303	4
2-Methyl-8-ethylquinoline	263	32
2,3-Dimethyl-8-ethylquinoline	300	39
2,4-Dimethyl-8-ethylquinoline	292-293	3
2,3,4-Trimethyl-8-ethylquinoline	320	30
2,3-Dimethyl-4,8-diethylquinoline	319	65
2,3,8-Trimethyl-4-ethylquinoline	310-311	31
2,3-Dimethyl-8- <i>n</i> -propylquinoline	300	4
2,4-Dimethyl-8- <i>n</i> -propylquinoline	292-293	5
2,3,4-Trimethyl-8- <i>n</i> -propylquinoline	330	62
2,3,4-Trimethyl-8-isopropylquinoline	327	64
2,3-Dimethyl-4-ethyl-8- <i>n</i> -propylquinoline	327	65
2,4-Dimethyl-8- <i>sec</i> -butylquinoline	310	63
2,3-Dimethyl-benzo(h)quinoline	365	66
2,4-Dimethyl-benzo(h)quinoline	355	66
2-(2,2,6-Trimethylcyclohexyl)-4,6-dimethylpyridine	279-284	69
<i>dl</i> - <i>sec</i> -Butyl-4,5-dimethylpyridine	214	58, 1
3- and 4-cyclopentylpyridine	210-213	43a

The quinoline bases extracted from California distillates contain methyl groups in the pyridine nucleus and in the benzene nucleus an alkyl group from methyl to butyl (and possibly higher), invariably at position 8. Quinoline homologs alkylated at positions 2, 3 and 8 predominate, whereas homologs alkylated at positions 2, 4 and 8 occur only in small amounts. Shive *et al.*⁶⁹ found that the base $C_{16}H_{25}N$ in kerosene extracted from California petroleum is a pyridine derivative with a cyclohexyl ring in the side chain.

The elucidation of the structure of non-aromatic bases is a very difficult problem because of the meager knowledge of such compounds. The naphthenic "kerobases" of formulas $C_{13}H_{21}N$ and $C_{16}H_{25}N$ were isolated from nitrogen bases occurring in California kerosene distillates,² but one of them was found to be semi-aromatic, consisting of a pyridine and a cyclohexyl ring ($C_{16}H_{25}N$).

In addition to quinoline homologs, Axe and Bailey,⁴ and Axe, Henson and Schuhard⁶ isolated from a California transformer oil nitrogen bases

of high specific gravity and refractive index, both aromatic and non-aromatic, and belonging mostly to the tricyclic type. The yield of the bases was as high as 0.75 per cent by volume of the solvent extract produced by the treatment of the transformer oil. Some of the high-boiling bases probably belong to the acridine or naphtho-quinoline groups. The empiric formulas of the bases are: $C_{15}H_{13}N$ and $C_{16}H_{15}N$.

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Chapter 9

Resins and Asphaltic Compounds

Classification and General Properties

The investigation of the chemical constitution of petroleum resins and asphalts is hindered by their amorphous nature. The constitution of these compounds is not at all clear, and they are classified chiefly on the basis of their physical properties. Marcusson²⁰ classified them as follows:

(1) Neutral resins, which are insoluble in alkalies and acids and completely miscible with petroleum oils, including light fractions (C_5 fraction).

(2) Asphaltenes, which are neutral and insoluble in light gasolines and petroleum ether. In contrast to the neutral resins, the asphaltenes are precipitated in the presence of an excess of petroleum ether. Both asphaltenes and neutral resins are completely soluble in benzene, chloroform and carbon disulfide.

(3) Asphaltogenic acids, which are soluble in alkaline solutions and in such solvents as benzene. Since these are present in petroleum in insignificant quantities, the neutral resins and asphaltenes are the most important resinous compounds of petroleum.

Carboids or "free carbon" are closely related to asphaltenes, from which they are readily formed at higher temperatures. Carboids are completely insoluble in benzene and similar solvents. They are absent in straight-run products but may occur in cracked residues and asphalts due to coke-formation, which occurs at high cracking temperatures.

Richardson²⁷ designated as *carbenes* the asphaltenes insoluble in carbon tetrachloride but soluble in benzene and chloroform. Asphaltenes of straight-run products are usually completely soluble in carbon tetrachloride. Cracked residues may contain a considerable proportion of carbenes; thus carbenes may be considered as an intermediate stage of condensation between asphaltenes and carboids.

The division of asphaltenes on the basis of their solubility in carbon tetrachloride is ambiguous and confusing. Hillman and Barnett¹⁴ showed that asphaltenes may be separated into a number of fractions, depending upon their solubility in various solvents. They dissolved asphaltenes, precipitated by isopentane, consecutively in a series of solvents of increasing polarity and obtained various fractions of asphaltenes. The solubility of the fractions in these solvents apparently depends upon the degree of condensation, which is maximum for

asphaltenes soluble in most polar solvents. Thus, the asphaltenes are non-homogeneous, but may be fractionated according to their degree of condensation. The carbenes, or asphaltenes insoluble in carbon tetrachloride, represent a wide range of asphaltenes, which may be separated into narrower fractions.

There is a close relation between asphaltenes, resins, and high molecular weight polycyclic aromatic hydrocarbons. The heavy polycyclic aromatics of petroleum, on oxidation gradually form neutral resins (and probably asphaltogenic acids, according to Marcusson); asphaltenes are formed as a result of further oxidation of neutral resins. On the contrary, the hydrogenation of asphaltic products containing neutral resins and asphaltenes produces heavy hydrocarbon oils, *i.e.*, neutral resins and asphaltenes are hydrogenated into polycyclic aromatic or hydroaromatic hydrocarbons. Thus, the polycyclic aromatic structure of neutral resins and asphaltenes is well established. They differ, however, from polycyclic aromatic hydrocarbons by the presence of oxygen and sulfur in varied amounts. The presence of nitrogen in some asphaltenes has been proved by Lane *et al.*¹³ and by Hillman and Barnett.¹⁴

The part played by oxygen, sulfur and nitrogen in formation of neutral resins and asphaltenes is not clear. The formation of oxygen- or sulfur-free resins and asphaltenes seems to be quite possible, for instance, from pure hydrocarbons free of oxygen, sulfur or nitrogen. Cracking of such hydrocarbons as paraffin wax or low molecular weight hydrocarbons yields in advanced stages condensation products which finally form resinous and asphaltic compounds. The presence of oxygen or sulfur seems to be a favorable but not a necessary condition for the formation of such compounds. The probable reactions involved will be discussed later (page 406).

Sachanen²⁹ found an important difference between the physical structure of asphaltenes and that of neutral resins. Asphaltenes are dispersed colloiddally in petroleum products due to peptization by adsorbed resins and heavy polycyclic hydrocarbons, whereas neutral resins form true solutions. According to him, the neutral resins are volatile and can be distilled with hydrocarbons. Each fraction of a crude (with the exception of gasoline and light kerosene) contains neutral resins of a molecular weight which is close to the average of the fraction. A typical molecule of a neutral resin differs from that of a hydrocarbon of the same fraction by the presence of 2 to 3 oxygen (sulfur) atoms.

Asphaltenes are non-volatile and have high molecular weights. Direct determination of the molecular weight of asphaltenes by conventional cryoscopic or ebullioscopic methods gives values up to 3,000. These low values are due unquestionably to the presence of adsorbed resins and hydrocarbons, which cannot be removed quantitatively from asphaltenes. Mack,¹⁹ and Eckert and Weetman^{7b} however, obtained comparatively moderate values for the molecular weight of asphaltenes by the viscosity method (Staudinger). The most interesting finding was the

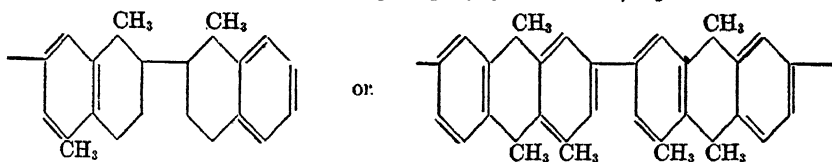
rapid decrease in the molecular weight with temperature. Thus, the molecular weight of 5,000 for an asphaltene at 0° fell to 1,800 at 120°. The asphaltenes are in true solution at this temperature. Other methods give higher values for the molecular weight of asphaltenes. Pfeiffer and Saal²⁴ determined the molecular weight by studying asphaltenic molecular films by Langmuir's method. They found the values of between 9,000 and 140,000. Swanson²⁴ gives values of the same order on the basis of other physical methods (diffusion and dielectric constant vs. frequency). Katz and Beu^{15a} examined petroleum asphalts and residues with the electron microscope and found that the asphaltene particles, if present, are less than 65 Å in diameter, corresponding to the molecular weight less than 90,000. Unfortunately, no attempts were made to determine the presence or percentage of asphaltenes in the products by the conventional method; they are almost entirely absent in straight-run residues from East Texas crude, studied by the authors.

As will be seen later, asphaltenes are dispersed in petroleum oils either colloiddally or in suspension, and are the cause of their heterogeneous structure, which occurs only in the presence of asphaltenes and petroleum waxes. While the asphaltenes bring about the colloidal or suspension structure, the excess of petroleum wax above saturation forms the microcrystalline structures discussed in Chapter 6. The popular idea of the colloidal or "isocolloidal" structure of all high-boiling petroleum fractions is entirely fallacious.

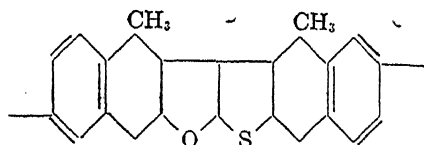
If the aromatic character of neutral resins and asphaltenes is certain, any particular data on the structure of these compounds are a matter of speculation. Marcusson²⁰ advanced the theory of the polycyclic structure of neutral resins and asphaltenes.

Hillman and Barnett¹⁴ pointed out that the completely condensed structure of resins and asphaltenes is improbable, since hydrocarbons of such a structure are insoluble in benzene, carbon disulfide and similar solvents, in which neutral resins and asphaltenes are highly soluble. In this respect, Clar's recent results are of particular interest. Clar⁵ synthesized hexacene and heptacene containing 6 and 7 aromatic condensed rings, respectively. Both hydrocarbons are colored; hexacene is dark green and heptacene is almost black, but both are only slightly soluble in aromatic hydrocarbons, as stated above. The dark, almost black color of heptacene, similar to that of neutral resins and asphaltenes, should be emphasized.

Hillman and Barnett suggested a chain structure for resins and asphaltenes, the chains consisting of polycyclic nuclei, *e.g.*:



The direct combination between the nuclei is shown in the above formulas, but the links of oxygen or sulfur atoms may be between the nuclei, as follows:



It should be borne in mind, however, that the above structural formulas given by Hillman and Barnett do not reflect the non-crystalline, amorphous nature of neutral resins and asphaltenes. The partially condensed polycyclic hydrocarbons are crystalline and also sparingly soluble in the solvents mentioned above. The links between the aromatic nuclei probably consist of such linear groups as $-\text{CH}_2-$, $-\text{CH}_2-\text{CH}_2-$, $-\text{CH}_2-\text{S}-$ etc. Such structures, even with polycyclic nuclei, have a resinous and amorphous character, like many synthetic resins and Buna-S. These products frequently have the same solubility characteristics, *i.e.*, are easily soluble in solvents with high surface tension but insoluble in solvents with low surface tension. The difference between the neutral resins and asphaltenes is apparently due mostly to the number of chains.

This hypothesis, close to that of Hillman and Barnett, satisfactorily explains the amorphous and resinous properties of neutral resins and asphaltenes by the chain structure and the chemical properties by the polycyclic and aromatic structure of the nuclei.

Methods of Separating Resinous and Asphaltic Compounds

As stated above, the classification of the resinous and asphaltic constituents is based upon their physical properties. Accordingly, various classes of these constituents are separated by various solvents, precipitating agents, or adsorbers. The only chemical method used is the action of alkaline solutions for separation of asphaltogenic acids and saponification of asphaltogenic anhydrides.

Determination of Carboids ("Free Coke").—The determination of carboids or "free coke" is based upon their insolubility in benzene or chloroform. A sample of the product to be tested is diluted with 50 to 100 volumes of benzene and allowed to stand for 12 hours. The carboids are insoluble in the original product, but usually form a fine suspension due partially to the high viscosity of products containing carboids, and partially to a certain peptizing effect of resins and heavy aromatic hydrocarbons. The dilution with benzene decreases the viscosity of the medium and simultaneously eliminates the peptizing action of resins easily soluble in benzene. The precipitated carboids are separated by filtration, washed repeatedly with benzene, and dried on a filter at 100°.

If the carboids were precipitated together with asphaltenes by pe-

troleum ether, the mixture of carboids and asphaltenes can also be separated by benzene. A weighed quantity of asphaltenes and carboids is dissolved in a large excess of benzene (*e.g.*, 100 parts by weight of benzene per part of the solids). The carboids undissolved in benzene are separated by filtration, as in the previous procedure.

Determination of Asphaltogenic Acids and Anhydrides.—The separation and determination of asphaltogenic acids is based on their solubility in alcohol. Ten grams of a petroleum product to be tested are precipitated with 100 cc of neutralized alcohol (96 per cent). If the product is solid or very viscous, it is dissolved in 25 cc of benzene. The mixture of alcohol and product is allowed to stand for at least 12 hours. The alcohol solution is decanted from the undissolved part, which is washed with alcohol. The alcohol solutions are combined and titrated with 0.1*N* alcoholic solution of potassium hydroxide with Alkaliblauf. The titrated solution is diluted with an equal volume of water, which precipitates the hydrocarbons and other compounds dissolved or/and emulsified in alcoholic solution. The hydrocarbons and compounds are extracted with benzene. The soap solution is separated and acidified with hydrochloric acid to precipitate free asphaltogenic acids, which are extracted with benzene. The benzene extract is separated and evaporated, leaving free asphaltogenic acids.

If the product contains naphthenic acids, the asphaltogenic acids will be determined and extracted with naphthenic acids. There are no reliable methods for separation of asphaltogenic acids from naphthenic acids of high molecular weight, the properties of which are not well known. A certain degree of separation may be obtained by the use of petroleum ether, which dissolves naphthenic acids, the asphaltogenic acids being insoluble.

In addition to asphaltogenic acids, some non-acidic compounds, which are saponified into soaps, may be present in heavy petroleum products. Marcusson considers the compounds as the anhydrides of asphaltogenic acids. The separation and determination of these anhydrides is performed as follows. The precipitate from the above alcoholic treatment of the petroleum product is mixed with the precipitate obtained from the soap of asphaltogenic acids after dilution with water. The mixture is saponified with 1.0*N* alcoholic potassium-hydroxide solution at boiling temperature, and allowed to stand for at least 6 hours. The soap solution is separated from the unsaponified product and treated with an equal amount of water to precipitate unsaponifiable products dissolved or emulsified in the alcohol solution. These are extracted with benzene and separated from the soap solution, which is acidified with hydrochloric acid. The asphaltogenic acids liberated are extracted with benzene. The benzene solution is evaporated to give free asphaltogenic acids, which were in the original product probably in the form of anhydrides.

The content of asphaltogenic acids and anhydrides in petroleum

products is usually very small, particularly in distillates; straight-run residues and asphalts contain from 0.5 to 1.0 per cent. The content of these compounds in natural asphaltic bitumens is much higher, amounting to 10 per cent. On the contrary, cracking residues do not contain any measurable amount of asphaltogenic acids or anhydrides.

Separation of Asphaltenes.—It is well known that low molecular weight paraffin hydrocarbons, such as pentanes, petroleum ether, etc., as well as ethyl ether, precipitate asphaltenes which are dispersed colloiddally in petroleum products. An excess of petroleum ether is used to effect complete separation of the asphaltenes. Sachanen²⁹ cleared up the mechanism of this process. The asphaltenes are lyophobic with respect to low molecular weight paraffin hydrocarbons and lyophilic with respect to aromatic hydrocarbons and resins. Both aromatic hydrocarbons and resins are readily adsorbed by asphaltenes. Having adsorbed the aromatic hydrocarbons and resins present in an oil product, the finely divided asphaltenes are dispersed in the product. Thus the resins and aromatic hydrocarbons function as peptizing agents which dissolve (colloidally) the asphaltenes. In the presence of an excess of low-boiling paraffin hydrocarbons, the adsorbed resins and aromatics are partially or completely dissolved in the solvent. As a result, the asphaltenes are depeptized, coagulated, and precipitated from the lyophobic solution.

Petroleum ether used for precipitation of asphaltenes should be aromatic-free and highly paraffinic; otherwise, naphthenes and particularly aromatics may have some peptizing effect on the asphaltenes. An excess of petroleum ether is essential; usually 30 to 40 volumes of petroleum ether per volume of the product are used for precipitation. In ASTM test D 91-35, 10 cc of the oil to be tested are mixed with 90 cc of petroleum naphtha, and the precipitate formed is measured by centrifuging in a graduated cylinder. The specifications of the naphtha are: 70° to 73° API, aniline point 58° to 60°, IBP not less than 50° (122°F), 50 per cent ASTM distillation at 70° to 80° (159° to 176°F), EP not more than 130° (260°F).

It should be mentioned that the ASTM determination has only a commercial value. In used oils not only asphaltenes but some acids as well are precipitated in this test. For a more complete precipitation of asphaltenes the petroleum ether must be lighter than that specified above; also a higher ratio of ether to petroleum oil must be used. The petroleum ether must consist predominantly of pentanes, hexanes and to a lesser degree of heptanes.

The separation and quantitative determination of asphaltenes is carried out as follows. The product left after the saponification of the anhydrides is dissolved, if necessary, in a small amount of benzene (10 cc) and precipitated with 400 cc of petroleum ether. The mixture is left for 12 hours and then the asphaltenes are filtered and washed with petroleum ether. They are dried at 100° and weighed on the filter. It should be mentioned that the content of asphaltogenic acids and an-

hydrides in petroleum residues and asphalts usually does not exceed 0.1-0.2 per cent. In such cases the preliminary separation of asphaltogenic acids and anhydrides may be omitted, and the product may be directly treated with petroleum ether for the separation of asphaltenes. If the product to be tested is solid or very viscous, it is dissolved in benzene (10 grams per 25 cc of benzene).

The percentage of asphaltenes determined by the precipitation depends on the boiling range of the petroleum ether or on the molecular weight of the paraffin hydrocarbons used for precipitation. Such paraffins as *n*-heptane or *n*-hexane, boiling in the range of petroleum ether, give figures for the content of asphaltenes close to those obtained with petroleum ether, whereas normal and isopentane precipitate about 25 to 50 per cent more. Ludeman¹⁷ found that the amount of the "sludge" precipitated with isopentane is 10 to 25 per cent more than that obtained with petroleum ether.

This can be expected because the low molecular weight paraffins are more lyophobic with reference to asphaltenes, and therefore separate them more completely. However, there is another phenomenon which interferes with the coagulation of asphaltenes and complicates their quantitative determination.

If still lower molecular weight paraffins are used for precipitating them, such as butane, propane, etc., the relative amount of the precipitation compounds increases enormously from pentanes to butane, from butane to propane, etc. The products precipitated by liquid propane, etc., however, are of quite different appearance from the asphaltenes. They become viscous and tacky, while pure asphaltenes are solid, dry powders. Neutral resins and high molecular weight aromatic hydrocarbons, completely miscible with all paraffins liquid at room temperature, are only partially soluble or insoluble in such liquid hydrocarbons as butane, propane, ethane, and methane. As a result, the dilution of a petroleum oil with butane, etc., causes precipitation of asphaltenes, as well as resins and high molecular-weight aromatics and naphthenes.

The interference of precipitated resins and heavy hydrocarbons with asphaltenes makes determination of the latter difficult. The solvent should completely precipitate the colloidal asphaltenes, but completely dissolve resins and hydrocarbons. So far the method of determining asphaltenes has not been perfected to the desired degree; thus the figures for content of asphaltenes are of only relative value, indicating how much precipitated material is formed by using a certain petroleum ether, pentane, or some other appropriate precipitating solvent. The figures obtained by precipitation with petroleum ether should be considered as a low limit of the asphaltene content; those obtained with butane are too high and include a considerable proportion of resins and perhaps of heavy hydrocarbons.

A further complication of the problem is the low solubility of solid paraffins, *i.e.*, of petroleum wax in the solvents at low and moderate

temperatures. In such cases, in which petroleum wax is precipitated with asphaltenes, the wax is removed by repeated treatments with such hydrocarbons as pentane or petroleum ether. The paraffin wax is dissolved in the hydrocarbons according to its solubility at a given temperature, and can be removed completely by a number of treatments with a sufficient volume of the solvent.

As has been discussed above, the asphaltenes are not homogeneous, and may be separated into fractions of different solubility in various solvents. Hillman and Barnett¹⁴ dissolved asphaltenes in the following solvents of increasing polarity: hexane, carbon tetrachloride, benzene, carbon disulfide and pyridine. As a result, the asphaltenes were separated into five fractions. The first fraction soluble in hexane, however, apparently consisted mostly of neutral resins adsorbed by asphaltenes.

The separation of carbenes or asphaltenes insoluble in carbon tetrachloride can be effected by treating the asphaltenes with an excess of carbon tetrachloride. The part insoluble in this solvent represents carbenes.

Separation of Neutral Resins

After the removal of asphaltenes (and asphaltogenic acids, if present) neutral resins can be separated from hydrocarbons by adsorption.

Any active adsorber can be used for adsorption and separation of neutral resins which have a polar character and are much more readily adsorbed than hydrocarbons. Floridin and silica gel are usually employed for this purpose. Floridin has some condensation effect upon the neutral resins which, having been recovered, become insoluble in petroleum ether and other petroleum oils. Silica gel has no such effect, however. Garner⁸ adsorbed neutral resins on animal charcoal.

The neutral resins adsorbed by silica gel or floridin are recoverable by extraction in Soxhlets, either with benzene or, better, with benzene-alcohol (50:50). Gurwitch¹² showed that the mixture of benzene and alcohol quantitatively extracts the neutral resins because of the action of alcohol, which is adsorbed more readily than the neutral resins and thus ejects them from the surface of the adsorbent. Strieter³³ recommended the use of ethyl ether for the extraction of resins. The separation and determination of neutral resins is a conventional operation and cannot be considered as a quantitative determination. There is no sharp distinction between neutral resins and hydrocarbons with reference to adsorption. Furthermore, the adsorption of neutral resins is not entirely selective; some high molecular weight aromatic hydrocarbons may be adsorbed almost as readily as some neutral resins. For this reason, the figures for the content of neutral resins can be considered as relative, depending on the conditions of adsorption. With the same adsorbent the percentage of neutral resins depends upon the relative amount of adsorbent as well as upon the conditions of washing the hydrocarbons from

it. All conditions of the analysis must be the same to produce comparable results for various oil products.

On the other hand, the data of Haus¹³ show that the separation of resins from hydrocarbons by adsorbents is unexpectedly sharp. He oxidized a paraffinic and a naphthenic oil under various conditions at 150° to 250° for periods of from 6 to 200 hours. The oils regenerated after the separation of resins (and other asphaltic materials) by floridin were practically identical. For instance, Table 140 summarizes the data of the ultimate analysis of the oils after the separation of resins. The data pertain to the paraffinic oil.

Table 140. Ultimate Analysis of Oxidized Oils After Separation of Resins.

	6 hours at 150°	200 hours at 150°	6 hours at 200°	100 hours at 200°	56 hours at 250°
Carbon	86.74	86.74	86.83	86.60	86.16
Hydrogen	12.34	12.57	12.25	12.66	12.75
Sulfur	0.77	0.50	0.60	0.47	0.46
Oxygen	0.15	0.19	0.32	0.27	0.63

Notwithstanding the quite broad variations in temperature and time of oxidation, the unoxidized and unresinified oils were practically the same. Thus, the oxidation and resinification of petroleum hydrocarbons under various conditions yields resinous and asphaltic products which have quite different adsorption properties from the oils, and which can be sharply separated by adsorption.

The procedure for determining neutral resins is as follows. After removal of asphaltenes, the filtrate containing neutral resins, oils, and petroleum ether is evaporated until about 100 cc of solution are left. The solution is treated with 50 grams of floridin or 100 grams of silica gel. The treatment is carried out at room temperature for 12 hours. The solution is completely decolorized after the treatment. The adsorbent with adsorbed neutral resins is placed in a Soxhlet and first treated with a light gasoline fraction boiling between 50° and 80° to wash out hydrocarbons; this gasoline fraction may also partially extract a small amount of neutral resins, indicated by the yellowish color of the washing gasoline. In such cases the gasoline used for washing is repeatedly treated with fresh adsorbent. After washing, the gasoline is replaced by benzene-alcohol which extracts neutral resins in the same Soxhlet. When the extraction is complete, the solution of neutral resins is evaporated and the neutral resins are dried at 100° and weighed.

Poll²⁸ modified the Marcusson method of analysis as follows. The oil product is treated with an excess of petroleum ether in the usual manner. The solution filtered from asphaltenes is treated with an amount of active clay sufficient for almost complete discoloration of the solution. The solution is filtered and the clay is washed with petroleum ether. The petroleum ether solution is evaporated and leaves the oils. The clay is repeatedly extracted with chloroform. The combined extract is evaporated and gives "petroleum resins." After this operation the

clay contains asphaltic compounds; it is mixed with the chloroform solution of the asphaltenes separated by petroleum ether until all the asphaltenes are adsorbed. The clay is then extracted with pyridine at room temperature. On evaporation, the extract gives "asphaltic resins." The clay containing unextracted materials is treated with pyridine and carbon disulfide (1:1 by volume); after evaporation this extract gives "hard asphalt."

The comparison of this method with the Marcusson method shows that the separation of oils is practically the same in both. The separation and determination of "petroleum resins" is close to that of "neutral resins" by Marcusson. The separation of "asphaltic resins" and "hard asphalt" differs from the determination of asphaltenes. It is not believed that the Poll method has any advantage; on the contrary, the separation of asphaltic resins and asphalts after adsorption may involve the condensation process, which partially condenses resinous constituents soluble in oils into asphaltic compounds, such as asphaltenes, which are insoluble in oils.

Hoiberg and Garriss¹⁴ suggested separating "hard resins" with 80 per cent isobutyl alcohol and 20 per cent cyclohexane, and "soft resins," after the separation of petroleum wax, with isobutyl alcohol. The method similar to the old method by Holde (ethyl alcohol and ether) has the general shortcoming of using an arbitrary mixture of two solvents. Thus the difference between the hard and soft resins is quite arbitrary, depending upon the proportion of the two solvents.

Separation of Neutral Resins and Asphaltenes by Liquefied Gases

It has been stated that liquid propane and butanes precipitate not only asphaltenes but also neutral resins and to some extent heavy hydrocarbons. Bray, Swift and Carr⁴ treated a Poso Creek residuum with 10 volumes of various liquid hydrocarbons of low molecular weight at 80°F. The results are summarized as follows:

Hydrocarbon	Part insoluble hydrocarbon by vol.)	Sp. gr. of insoluble	M. P. of insoluble (°F)
Ethane	89.0	0.98	liquid
Propane	25.0	1.063	176
Butane	11.2		307
Pentane	4.8		320
Hexane	2.0		325

Liquid ethane precipitates most of the hydrocarbons. The action of liquid propane and butane is somewhat more selective; these hydrocarbons precipitate asphaltenes, neutral resins, and the heaviest hydrocarbons.

The precipitating power of each liquid hydrocarbon, for instance, propane, changes with temperature; the higher the temperature, the greater the percentage of precipitate. As a result, at temperatures close to the critical, propane would precipitate most of the heavier oils, as

Wilson, Keith and Haylett³⁸ reported. A more or less selective precipitation and separation of neutral resins (and asphaltenes, if present) by liquid propane takes place at temperatures not exceeding 70° (158° F).

Not only gaseous hydrocarbons, but all other low molecular weight gases, such as carbon dioxide, hydrogen etc., can be used under certain pressures and temperatures for the precipitation of high molecular weight constituents. Pilat and Godlewicz²⁵ showed that the process of precipitation of high molecular weight aromatics, naphthenes, and resins can be performed by the use of the above gaseous hydrocarbons under correspondingly high pressures. The use of gaseous low molecular weight hydrocarbons above the critical temperature should even be preferred, since the solubility of heavy naphthenes and aromatics in liquid propane, etc., is lowest at temperatures close to the critical.

The separating effect of liquefied hydrocarbons is not selective: asphaltenes and neutral resins are precipitated with heavy hydrocarbons. Unfortunately, experiments are lacking which would correlate the analytical data produced by the Marcusson method with those obtained by treatment with liquefied gases. Apparently the treatment with liquid propane at room temperature, followed by washing of the insoluble part with the same solvent, produces fairly pure neutral resins from distillates and asphaltenes and resins from residues. Graff and Forrest¹⁰ treated a Santa Fé Springs heavy distillate (A.P.I. gravity 15.7, Saybolt viscosity at 210°F 400, and Conradson carbon 4.3 per cent) with 10 volumes of propane at 100°F and then washed the insoluble part with 3 volumes of propane at the same temperature. As a result, 13 per cent of resins was separated. The properties of the resins were: specific gravity 1.045, melting point 170°F, molecular weight 590, and percentage of sulfonatable constituents 90. The product separated apparently consisted predominantly of neutral resins. The treatment of a Mid-Continent residuum (A.P.I. gravity 19.2, viscosity at 210°F 306 and Conradson carbon 7.4 per cent) under the same conditions produced 10.9 per cent of "asphalt" containing 13.7 per cent of asphaltenes (insoluble in naphtha).

Separation by Polar Solvents

Another method of the non-selective separation of asphaltenes and neutral resins is treatment with an appropriate solvent of the type of liquid sulfur dioxide, phenol, nitrobenzene, etc. Solvents of the polar type extract asphaltenes, neutral resins, various acids, sulfur compounds, and aromatic hydrocarbons, which are readily soluble in these solvents. As a result, the separation of asphaltenes and neutral resins is not selective at all. In addition, separation of the latter is not complete, since they are merely distributed between the extract and raffinate; they are, however, concentrated in the extract.

In view of the action of the low molecular weight paraffins discussed above, this may contribute to the action of the polar solvents. Thus, for instance, liquid propane may be used with phenol or cresylic acid (the

Duosol process). As a result, the separation of asphaltenes and neutral resins, as well as of aromatics, is much more complete than with cresylic acid alone. The Duosol process is also non-selective with respect to the asphaltenes and resins, which are separated with aromatic hydrocarbons and oxygen and sulfur compounds.

Solvent extraction can be successfully used for a preliminary separation of asphaltenes and resins. For instance, Rossini²⁸ described the following procedure. A lubricating fraction of a Mid-Continent crude was dewaxed and then treated with liquid sulfur dioxide at 40°. The solvent extracted 21 per cent of the original fraction. As might be expected, the extract consisted of aromatic hydrocarbons, various sulfur and oxygen compounds, and asphaltic and resinous constituents.

A further separation of resins ("asphaltic portion") from other constituents was performed by treating the extract in liquid sulfur dioxide at 55° with petroleum ether; this extracted a "petroleum ether-soluble portion," which was mostly cyclic hydrocarbons. The separation of the hydrocarbons, of course, was not very sharp. As a result, the "extract portion" (*i.e.*, the portion extracted by petroleum ether and the silica gel hold up of the oil after extraction with sulfur dioxide) contained about 0.9 per cent sulfur, 0.1 per cent nitrogen, and 0.5 per cent oxygen. In any case, the semi-solid "asphaltic portion" included most of the asphaltic and resinous substances of the original lubricating fraction.

Less polar substances, such as acetone or alcohols, may be used for extraction of lighter neutral resins from distillates, as will be seen later. On the other hand, heavy neutral resins and asphaltenes are insoluble in these solvents, in the excess of which the hydrocarbons are also soluble. Thus, the hydrocarbons and lighter neutral resins are extracted with acetone until all the soluble part is removed. The residuum consists of asphaltenes and heavy resins. Lane, Nelson, Devine and Smith¹⁸ reported on the separation of "asphalt" by this method for various crudes. The "asphalt" has a specific gravity of 1.18 to 1.34 and an elemental composition corresponding to the mixture of asphaltenes and neutral resins.

Properties of Neutral Resins

Our knowledge of the neutral resins is very limited. Extracted by an adsorbent and recovered, they are sticky or solid materials colored deeply red in thin layers. Resins of lower molecular weights are less colored than the heavier ones. "Colorless" or light-colored resins or plastics may be produced by preliminary separation of asphaltenes and deeply colored heavy neutral resins, with subsequent precipitation of the light-colored neutral resins. Laughlin and Cier^{18a}, *e.g.*, produce such "asphalts" or resins by precipitating heavy asphaltic residues with liquid butane and by second precipitation of light-colored resins with propane. The neutral resins do not crystallize, and thus cannot be separated into individual components.

Sachanen and Wassilieff³⁰ isolated neutral resins from various fractions of a crude oil, from kerosene to heavy residuum. The oil fractions were treated with petroleum ether (if necessary) and sodium hydroxide solution for removing asphaltenes and various acids. Then the neutral resins were adsorbed by silica gel, from which they were extracted with alcohol and benzene. The properties of the neutral resins are given in Table 141. Each fraction gives the resins which are specific for the fraction. The average molecular weight of a neutral resin is close to that of the fraction, exceeding it usually by 30 to 40. The formulas of the neutral resins include from two to three oxygen atoms, whereas the content of sulfur was not sufficient to account for one sulfur atom, and thus was added to the oxygen content. A low sulfur content has been found for neutral resins separated from crudes poor in sulfur. It is certain, however, that the neutral resins of crudes rich in sulfur have a high sulfur content.

Table 141. Empirical Formulas of Neutral Resins Separated from Crude Oils, Distillates, and Residues.

Oil Product	Ultimate Analysis (%)				Mol. Weight	Formula	Series
	C	H	S	O			
<i>Light Asphaltic Crude Oil</i>							
Crude oil	84.14	9.77	0.79	5.30	589	$C_{41}H_{57}O_2$	$C_nH_{2n-24}O_2$
Kerosene	77.90	9.97	1.80	10.33	290	$C_{15}H_{25}O_2$	$C_nH_{2n-10}O_2$
Gas oil	80.92	9.92	1.56	7.60	319	$C_{22}H_{31}O_2$	$C_nH_{2n-12}O_2$
Non-visc. dist.	82.20	10.22	1.26	6.23	466	$C_{32}H_{47}O_2$	$C_nH_{2n-16}O_2$
Viscous dist.	82.62	10.06	1.17	6.15	471	$C_{32}H_{47}O_2$	$C_nH_{2n-16}O_2$
Residuum	84.75	9.75	0.51	4.99	757	$C_{53}H_{73}O_3$	$C_nH_{2n-32}O_2$
Blown asphalt	84.12	9.92	0.64	5.32	788	$C_{53}H_{77}O_3$	$C_nH_{2n-32}O_3$
<i>Light Naphthenic Crude Oil</i>							
Crude oil	83.48	10.42	0.75	5.35	738	$C_{31}H_{76}O_2$	$C_nH_{2n-26}O_2$
Kerosene	78.70	9.61	1.73	9.96	278	$C_{16}H_{26}O_2$	$C_nH_{2n-10}O_2$
Gas oil	77.85	9.75	3.68	8.72	327	$C_{21}H_{35}O_2$	$C_nH_{2n-10}O_2$
Heavy gas oil	79.68	9.71	2.56	8.05	361	$C_{24}H_{39}O_2$	$C_nH_{2n-14}O_2$
Viscous dist.	81.54	9.64	1.00	7.82	446	$C_{30}H_{42}O_2$	$C_nH_{2n-18}O_2$
Hvy. visc. dis.	82.94	9.76	1.08	6.22	514	$C_{35}H_{50}O_2$	$C_nH_{2n-20}O_2$
Residuum	85.28	10.26	0.40	4.06	969	$C_{59}H_{95}O_2$	$C_nH_{2n-40}O_2$

The isolation of neutral resins from distillates shows that the former are volatile and are distilled with corresponding hydrocarbons. The close relation between the molecular weight of neutral resins and hydrocarbons of the same fraction shows that neutral resins are formed as a result of oxidation of some polycyclic hydrocarbons. As stated in the previous chapter, neutral resins are readily formed on oxidation of oil products rich in polycyclic hydrocarbons, under laboratory conditions. The series formulas of Table 141 show clearly that the ring structures of neutral resins of the same molecular weight, extracted from the two different crudes, are very similar.

As discussed above, neutral resins are highly polycyclic compounds; the number of rings and the length of paraffinic side or intercyclic chains is not known. The number of paraffinic carbon atoms in the side chains should be small in view of the high specific gravity and refractive index

of neutral resins. Thus, the number of rings in a molecule should be great, from 3 for the "kerosene" neutral resins to 10 or more for those separated from heavy residues. At least some of the rings should be aromatic, since the neutral resins, particularly the lighter ones, are easily soluble in sulfuric acid, forming sulfonic acids.

Hillman and Barnett¹⁴ analyzed the neutral resins by the Waterman method and found that they contain mostly aromatic rings and 40 to 45 per cent paraffinic side chains. The details of the analysis and calculations, however, have not been given.

The position of oxygen and sulfur (or nitrogen) atoms in molecules of neutral resins is completely unknown. According to Marcusson, these atoms are located in the rings, forming bridges. As mentioned above, the location of the oxygen and sulfur atoms in the links between the aromatic nuclei seems to be probable.

The iodine numbers of neutral resins are between 30 and 50, corresponding approximately to one double bond in the molecule. The presence of double bonds in neutral resins, however, has not been proved, and the iodine numbers may be due to some substitution reactions.

Table 141 contains the data on the neutral resins preformed in a crude oil. Haus¹³ separated the resins from a paraffinic and a naphthenic oil after oxidation at 150° to 250°, for 6 to 200 hours. The method of separation of these resins (Poll) differs somewhat from that used by Sachanen and Wassilieff. Some selected data are given in Table 142.

Table 142. Ultimate Analysis of Resins Produced by Oxidation.

Conditions of oxidation	150°, 6 hrs	150°, 50 hrs	150°, 200 hrs	200°, 6 hrs	200°, 100 hrs	250°, 6 hrs	250°, 25 hrs
<i>From Paraffinic Oil</i>							
C (%)	81.75	81.54	79.65	81.86	80.28	80.64	82.54
H	10.07	9.48	9.04	9.58	9.39	9.28	9.34
S	3.49	3.01	2.33	2.46	1.41	1.71	1.14
O	4.69	5.97	8.98	6.10	8.92	8.37	6.98
Mol. Wt.	550			510	540	545	660
<i>From Naphthenic Oil</i>							
C (%)	81.86	80.90	79.69	78.61	79.69	83.41	81.49
H	9.70	9.26	8.91	9.02	9.76	9.38	9.20
S	2.45	2.06	1.36	1.68	0.65	1.14	0.54
O	5.99	7.78	10.04	10.69	9.90	6.07	8.77
Mol. Wt.	453			506	540	590	650

Comparison of the data of Tables 141 and 142 leads to the rather unexpected conclusion that the neutral resins preformed and separated from lubricating distillates and those formed as a result of the oxidation of lubricating oils have comparatively close values of molecular weight and elemental composition, particularly in view of the different origin of the lubricating distillates. Thus, the virgin resins separated from the viscous distillates of Table 141 and the resins produced by oxidation of lubricating oils of Table 142 have a molecular weight of about 500, a carbon content close to 80 per cent, a hydrogen content of about 10 per cent, and a total oxygen and sulfur content near 8 per cent.

The fact that neutral resins, as well as asphaltenes, are formed as a result of oxidation of polycyclic hydrocarbons has been well established, as shown above. On the other hand, resins (and asphaltenes) can be converted into cyclic hydrocarbons by hydrogenation. The catalytic hydrogenation of heavy residues, as well as of asphalts, containing a large proportion of resins and asphaltenes under moderate temperature conditions produces moderate yields of gasoline, gas oil and heavy oils; the latter are formed by destructive hydrogenation of heavy hydrocarbons, resins, and asphaltenes. The oils formed do not contain an appreciable amount of sulfur or oxygen, which were split from the resins and asphaltenes in the form of hydrogen sulfide and water.

Thus, the close relationship between polycyclic hydrocarbons and neutral resins (or asphaltenes) can be proved by oxidizing these hydrocarbons into neutral resins and asphaltenes, as well as by reducing resins and asphaltenes into cyclic hydrocarbons by hydrogenation.

The neutral resins are completely miscible with most liquid petroleum products. The separation of neutral resins from asphaltenes is based upon the complete solubility of neutral resins in petroleum ether, in contrast to asphaltenes, which are precipitated by the ether. However, neutral resins are insoluble or sparingly soluble in liquefied gaseous hydrocarbons, such as propane etc., as discussed above. The solubility of neutral resins in such solvents as alcohol or acetone is slight, but is appreciable for the lighter neutral resins separated from light distillates. It explains the fact that Holde and Eickmann,¹⁵ Schwartz and Marcusson²¹ and others extracted a portion of the resinous material from heavy hydrocarbons by alcohol or acetone. Sachanen and Vassilieff³⁰ showed that neutral resins form true (non-colloidal) solutions in petroleum oils. The comparatively moderate values of molecular weight of neutral resins are in accordance with these conclusions. These authors give the following data on the solubility of a neutral resin extracted from a heavy crude in isoamyl alcohol:

Temp. (°C)	Conc. of saturated solution (gr./100 gr. of alcohol)
33	0.10
42	0.21
47	0.31
57	0.41
63	0.61
72	0.97
73	1.34
78	2.00

As mentioned above, the solubility of lighter neutral resins extracted from gas oil or lubricating distillates is much greater than the values given above.

The color of oil distillates depends almost entirely upon the presence of neutral resins, which are deeply colored. It should be remembered that asphaltenes, due to their involatility, are entirely absent in oil distillates, at least those that are freshly distilled.

Properties of Asphaltenes

The knowledge of the chemical constitution of asphaltenes, as of neutral resins, is very meager. As will be seen later, the ultimate analysis of asphaltenes is very close to that of neutral resins. In addition to this, the transformation of neutral resins into asphaltenes is a very easy process, which may proceed even at low temperatures. At elevated temperatures, particularly in the presence of air or oxygen, neutral resins are readily converted to asphaltenes. Thus the chemical structure of asphaltenes and neutral resins should be more or less similar. The principal differences between neutral resins and asphaltenes lie in their physical and physico-chemical properties. The molecular weight of asphaltenes is very high.

In conjunction with this, asphaltenes form colloidal solutions or suspensions in petroleum oils, depending upon the oil. Asphaltenes are lyophilic with respect to aromatics, in which they form highly dispersed colloidal solutions. Asphaltenes are lyophobic with respect to paraffins, particularly those of low molecular weight, such as pentanes, and petroleum ether. Thus the degree of dispersion of asphaltenes in petroleum oils depends upon the chemical composition of the latter. In heavy highly aromatic products the asphaltenes are colloiddally dispersed; but in the presence of an excess of petroleum ether and similar paraffinic hydrocarbons they are coagulated and precipitated. The process is reversible. The coagulated and precipitated asphaltenes can be peptized by the addition of aromatics and can be colloiddally dispersed, if the concentration of the aromatics is sufficient. Neutral resins are particularly effective as peptizers. Such compounds as resins or high molecular weight aromatics are readily adsorbed by asphaltenes and act as protective layers, isolating the colloidal particles from the coagulative action of lyophobic constituents of petroleum oils. If the proportion of the peptizing constituents in a petroleum oil is insufficient, the asphaltenes form more or less stable suspensions, depending on the proportion of the peptizing constituents.

Sachanen²⁹ showed that the solution of asphaltenes in an aromatic solvent is preceded by swelling of the powdered asphaltenes. This process is accompanied by evolution of heat.

Nellensteyn^{22, 23} found that the peptizing or precipitating properties of different liquids with respect to asphaltenes are closely related to the surface tension. Precipitation (flocculation) occurs when the solvent has a surface tension below 24 dynes/cm at 25°. Total peptization takes place when the surface tension exceeds 26 dynes/cm. In the intermediate zone between 24 and 26 dynes/cm, either flocculation or peptization may occur, depending on the properties of the asphaltenes. The table on page 401 summarizes the properties of various solvents.

The asphaltene particles are electrically charged and thus can be precipitated by application of an electrical potential or by flow of the

asphaltene-containing product through the sand, due apparently to electrical effects resulting from the flow. On the contrary, application of a counter-potential may prevent precipitation of asphaltenes from the crude oil flowing through a porous material (Dykstra, Beu and Katz^{7a}).

Liquid	Surface tension at 25°	Character of liquid
Pentane	13.5	Precipitating
Ether	16.7	
<i>n</i> -Hexane	17.0	
<i>n</i> -Heptane	18.6	
Carbon tetrachloride	25.4	Intermediate
Cyclohexane	25.7	
Chloroform	26.2	
Benzene	27.7	
Toluene	28.4	Peptizing
<i>p</i> -Xylene	29.1	
Carbon disulfide	30.6	
Pyridine	34.9	
Nitrobenzene	42.5	

The conception given above of the structure of asphaltenes or their colloidal solutions is based on the assumption that they are high molecular weight compounds containing carbon, hydrogen, oxygen, sulfur and nitrogen.

Another conception was developed by Nellensteyn, who assumed that asphaltenes consist of ultramicroscopic particles of elemental carbon protected or peptized by resins and highly unsaturated hydrocarbons, often with a high content of sulfur. The adsorption of the resins, etc., by elemental carbon is so strong that treatment with lyophobic solvents cannot separate the carbon from the adsorbed constituents. Nellensteyn,²² however, reported that the asphaltenes precipitated from a Mexican asphaltic bitumen had been extracted during one year with ether and had become partly insoluble in carbon tetrachloride or disulfide (no quantitative data are available). The x-ray diagram of the asphaltenes showed that the principal lines corresponded to those of graphite. Another proof of the Nellensteyn's hypothesis is the oxidation of asphaltenes with potassium permanganate, which gives the same oxidation products as those obtained with graphite, i.e., mellitic acid and various asphaltic products.

It should be pointed out that the experimental data supporting the Nellensteyn hypothesis are not convincing. The lines corresponding to the lines of graphite in x-ray diagrams, as well as the formation of mellitic acid (in an unknown yield) on oxidation of asphaltenes evidently cannot be considered as a support of the elemental structure of asphaltenes. Moreover, Nellensteyn states that the lines in the asphaltene x-ray diagram are feeble, and that only a part of the carbon in asphaltenes is graphitic. There are many data which are in disagreement with this theory. The neutral resins have moderate molecular weights and can be distilled without decomposition, so that the existence of free carbon in these compounds cannot be postulated. As has been stated above,

neutral resins are transformed into asphaltenes very easily even at room temperature or at slightly elevated temperatures. The formation of elemental carbon from the neutral resins at low temperatures seems hardly probable.

The easy hydrogenation of asphaltenes into hydrocarbons is an additional proof that graphitic carbon is lacking in asphaltenes. Gruse and Stevens¹¹ pointed out that the experiments on the diffusion and dialysis of asphaltene solutions are in disagreement with Nellensteyn's conception of colloiddally dispersed carbon. It may be added that, according to modern theories, coals also do not contain elemental carbon, but rather consist of various complex carbon compounds.

Thus, it seems much more probable and in better conformity with the present state of our knowledge that the asphaltenes are high molecular weight organic compounds rather than elemental carbon peptized by certain constituents. It should be remembered, however, that the peptization of asphaltenes by resins and high molecular weight aromatics has also been postulated by the first theory, so that the difference between the two theories lies mostly in the structure of the central parts of the dispersed particles or micelles of the asphaltenes. According to the first theory, the central part of the asphaltene micelle consists of high molecular weight compounds surrounded and peptized by neutral resins or aromatic hydrocarbons, whereas, according to the second theory, the central part of the asphaltene micelle is elemental carbon peptized by the same constituents.

Asphaltenes are not crystallized and cannot be separated into individual compounds or narrow fractions. Thus, the ultimate analysis is not very significant, particularly taking into consideration that the neutral resins are strongly adsorbed by asphaltenes and probably cannot be quantitatively separated from them.

The analytical data on the elemental composition of asphaltenes are meager. The elemental composition of asphaltenes from various sources may differ to a great extent, particularly with respect to sulfur content.

Thurston and Knowles³⁵ give the data shown in Table 143 on the elemental composition of various asphaltenes. Table 144 represents the data on the elemental composition of asphaltenes separated from a Cali-

Table 143. Ultimate Analysis of Asphaltenes.

	Origin				
	Soft Mexican asphalt, penetration 238	Blown Mexican asphalt m.p. 104.4°	Vacuum reduced Mexican asphalt m.p. 93.3°	Blown Gulf asphalt m.p. 93.9°	Blown cracked asphalt m.p. 93.9°
Carbon (%)	79.61	81.31	79.70	83.99	85.48
Hydrogen (%)	7.79	7.91	7.83	8.26	10.14
Ratio C:H	10.2	10.4	10.2	10.2	8.4
Sulfur (%)	8.09	7.79	8.25	1.70	0.56
Ash (%)	0.59	0.24	0.34	1.25	0.19
Oxygen (%)	3.92	2.75	3.88	4.80	3.63

fornia straight-run residuum, according to Hillman and Barnett,¹⁴ by the procedure described at the beginning of this chapter. The nitrogen content of asphaltenes of California origin is high—much greater than that of sulfur. Comparison shows that the composition of asphaltenes poor in sulfur (Thurston and Knowles, Hillman and Barnett, Sachanen) is fairly uniform: carbon 85-86 per cent and hydrogen 6-7 per cent. Asphaltenes rich in sulfur contain less carbon.

Table 144. Ultimate Analysis of Asphaltenes.

Fraction of asphaltenes soluble in	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulfur (%)	Oxygen (%)
Carbon tetrachloride	83.9	6.2	2.2	0.3	6.7
Benzene	86.8	6.1	2.3	0.8	3.7
Carbon disulfide	87.1	6.0	2.1	0.9	3.7
Pyridine	83.7	5.6	3.2	0.9	6.3

The asphaltenes from natural asphalts may be oxygen-free. In these sulfur completely replaces oxygen. Richardson²⁷ gives the following analysis of asphaltenes separated from natural Trinidad asphalt:

Carbon	82.0%
Hydrogen	7.8%
Sulfur	10.9%

In some cases properties and the ultimate analysis data for asphaltenes produced from the same source are independent of the conditions under which the product was formed. The following data²⁹ relate to the asphaltenes separated from a light reduced asphaltic crude, from the heavy residuum of the same crude, and from the blown asphalt produced from the heavy residuum:

Asphaltenes from	Sp. gr.	Iodine No.	C (%)	H (%)	S (%)	O (%)
Reduced crude oil			85.2	7.4	0.7	6.7
Heavy residuum	1.14	59	86.7	6.8	0.6	5.9
Blown asphalt	1.14	53	85.3	6.4	0.6	7.7

Taking into consideration the difficulties connected with the separation of pure asphaltenes, it may be concluded that the data given above are practically identical. It is to be pointed out that the asphaltenes of the blown asphalt are mostly newly formed as compared with the virgin asphaltenes of the reduced crude and residuum. It would be premature to generalize this result obtained for one crude oil and the blown asphalt from this crude.

Not much is known of the chemical properties of asphaltenes. On heating, they are not melted, but decompose, forming carbon and volatile products above 300°-400°. They react with sulfuric acid forming sulfonic acids, as might be expected on the basis of the polyaromatic structure of these compounds. The iodine number of the asphaltenes is comparatively high, from 40 to 60. Marcusson pointed out, however, that this fact does

not necessarily indicate the presence of double bonds, but is probably due to substitution reactions.

The color of dissolved asphaltenes is deep red at very low concentrations. Even such a low concentration in benzene as 0.0003 per cent makes the solution distinctly yellowish. The color of crude oils and residues is due to the combined effect of neutral resins and asphaltenes. The black color of some crude oils and residues is related to the presence of asphaltenes which are not properly peptized.

The coke-forming properties of petroleum products (Conradson and Ramsbottom carbon tests, A.S.T.M.-D 189-39 and D- 524-40 T, respectively) are also closely related to the content of neutral resins and asphaltenes. Hydrocarbons do not form an appreciable amount of coke under the conditions of the procedures used in the tests; neutral resins and asphaltenes are the coke-forming substances. Smith³² suggested that the carbon residue of a crude is roughly proportional to the percentage of asphalt present in it. To obtain the per cent of asphalt the carbon residue of the crude is multiplied by 2.5. The "asphalt" means the asphalt determined by treatment with acetone and consisting of asphaltenes and heavy neutral resins.

Vassilieff³⁶ showed that neutral resins extracted from crude oils by silica gel produce 20 per cent and asphaltenes about 70 per cent of coke in the Conradson test. Thus, the carbon residue of crude oils and residues may be calculated from the content of neutral resins and asphaltenes on the basis of the figures given above.

Table 145. Content of Neutral Resins and Asphaltenes in Crude Oils.

Crude oil	Sp. gr. 60°/60°F)	Neutral resins (% by wt)	Asphaltenes (% by wt)
Pennsylvania	0.805	1.5	0.0
Illinois, Loudon	0.835	12.0	
Oklahoma, Tonkawa	0.821	2.5	0.2
Oklahoma, Okla. City	0.835	5.0	0.1
Oklahoma, Seminole	0.830	7.0	
Oklahoma, Davenport	0.796	1.3	0.0
Texas, East	0.830	10.0	
Texas, West	0.870		1.7
Texas, Hould	0.936	12.0	0.5
Texas, Mexia	0.845	5.0	1.3
Louisiana, Rodessa	0.807	3.5	0.0
Gulf Coast, Mirando	0.925	4.5	
Calif., Santa Fé Springs	0.855	12.0	
Calif., Huntington Beach	0.897	19.0	4.0
Mexico, Poza Rica	0.873		2.4
Mexico, Panuco	0.988	26.0	12.5
Russia, Surachany	0.850	4.0	0.0
Russia, Balachany	0.867	6.0	0.5
Russia, Bibi-Eibat	0.865	9.0	0.3
Russia, Grozny (Wax-bearing)	0.844	5.5	0.9
Russia, Grozny (Wax-free)	0.860	8.0	1.5
Russia, Dossor	0.862	2.5	0.0
Russia, Kaluga	0.955	20.0	0.5
Asia, Burma	0.838	3.0	
Asia, Iraq (Kirkuk)	0.844	15.5	1.3
Asia, Iran	0.840	12.0	

Resins and Asphaltenes in Crude Oils and Distillates

The content of asphaltic compounds in crude oils depends largely upon the nature of the oils. Their specific gravity roughly indicates the relative amount of the asphaltic constituents, which are of a very high specific gravity, exceeding 1.0. Crude oils of low specific gravity are usually poor in asphaltic compounds, but in numerous cases they contain a considerable proportion of these products, which are masked by an excess of non-asphaltic light fractions. Crude oils of high specific gravity are on the average rich in asphaltic compounds. Table 145 contains systematized data on the content of asphaltenes and neutral resins in various crude oils. As mentioned above, the content of asphaltogenic acids and anhydrides in crude oils is insignificant (on the average less than 0.2 per cent). The data of Table 145 show that the total content of asphaltic compounds in crude oils varies within very broad limits, from 1 to 40 per cent, and the asphaltenes from 0 to 15 per cent.

Table 146 gives the data on the content of neutral resins and asphaltenes in various fractions of crude oil.

Table 146. Content of Asphaltic Constituents in Distillates of Balachany Crude Oil.

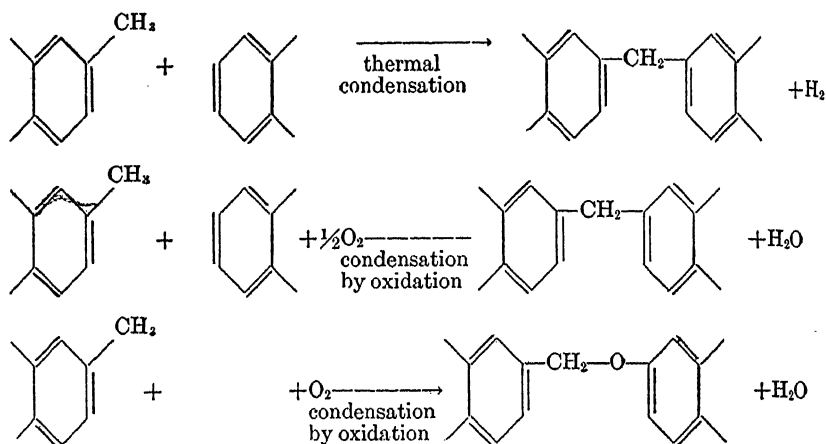
	Asphaltenes		Neutral resins	
	on fraction (% by wt)	on crude oil	on fraction (% by wt)	on crude oil
Crude oil		0.5		5.96
Gasoline	0.0	0.0	0.0	0.0
Kerosine distillate	0.0	0.0	0.20	0.06
Gas oil light	0.0	0.0	0.35	0.01
Gas oil heavy	0.0	0.0	1.19	0.23
Viscous distillate	0.0	0.0	4.10	0.50
Heavy viscous distillate	0.0	0.0	9.8	0.20
Residuum	2.1	0.6	19.8	4.96

The data of Table 146 show that the percentage of neutral resins in fractions increases rapidly with the boiling range of the fractions. The resins are concentrated in the residuum, which contains about 80 per cent of the total. The distillates do not contain asphaltenes which, being non-volatile, are completely concentrated in the residuum. A low content of asphaltenes in a distillate proves that the distillate was exposed to air for a period of time and at a temperature which were sufficient to effect a further oxidation of neutral resins to asphaltenes.

The content of asphaltic compounds in the total cracked product is usually greater than in the charging stock, because the condensation process results in the formation of highly polycyclic aromatic hydrocarbons, which finally produce resins, asphaltenes, and coke. Thus the percentage of asphaltic components in a cracked crude or residuum depends largely on the aromaticity of the charging stock. It should be kept in mind, however, that aromatic hydrocarbons are gradually formed on cracking as a result of various secondary reactions. Therefore, asphaltic components can be produced even by cracking purely aliphatic hydrocarbons. Of course, the formation of asphaltic compounds from such

charging stocks by cracking takes place to a more moderate extent and under more severe conditions than from charging stocks rich in aromatics.

The formation of resins and asphaltenes on cracking seems to be a quite different process than the formation of these products by oxidation. However, the properties of resins and asphaltenes produced on cracking are very similar to those of the asphaltic compounds resulting from oxidation. The condensation process which occurs on the formation of asphaltic compounds can be brought about either by purely thermal reactions at high temperatures or by oxidation at moderate temperatures, as, for instance:



Thus, the condensation product formed by oxidation may or may not be oxygen-free.

Cracked residues may contain a greater or lesser proportion of carboids, which are formed as a result of further condensation of asphaltenes at high temperatures.

Solvent refining of petroleum products is a process in which raffinates or refined oils are separated from extracts containing asphaltic materials and cyclic (mostly aromatic) hydrocarbons. The so-called solvent tars are produced from the extracts after the separation of solvent. They usually contain a large percentage of asphaltic components (resins and asphaltenes) which may be as high as 50 per cent of the tar. The data on the composition of two solvent tars are summarized in Table 147.

Table 147. Composition of Solvent Tars.

Solvent	Product treated	ϕ/δ	Flash (°F)	Viscosity at		Asphal- tenes (%)	Neutr. resins (%)	Arom. hydr. (%)	Non- arom. hydr. (%)
Furfural	Penna neutral	0.920	350	353	99	0	11	59	30
Duosol*	M. C. Cylinder stock	1.01			1,623	1	29	55	12

*Propane and cresylic acid.

The tars produced from distillates or Pennsylvania and some Mid-Continental residual stocks may contain a large proportion of neutral resins and no (or very little) asphaltenes.

Petroleum Asphalts

Petroleum asphalts are either the straight-run residues of asphaltic crudes of proper consistency or the so-called "blown" asphalts produced by oxidation of straight-run residues which do not have a penetration suitable for commercial asphalts. As shown in a preceding section, the asphaltic constituents, resins and asphaltenes, are concentrated in distillation residues. The proportion of the asphaltic components in the residuum predetermines the physical and mechanical properties of the

Table 148. Sulfur Content in Asphalts.

Source	Per cent sulfur
Petroleum, California	1.4
Petroleum, Texas	2.7
Petroleum, Mexico	6.1
Petroleum, Venezuela	3.2
Petroleum, Argentina	0.6
Petroleum, Grozny	0.6
Petroleum, Baku	0.8
Petroleum, Romania	0.6
Petroleum, Poland	1.0
Natural, Syria	8.5
Natural, Sclenizza	7.6
Natural, Bermudez	4.6
Natural, Trinidad	6.7

asphalts, *i.e.*, melting or softening point, penetration and ductility. The asphaltenes cause the hardness and the resins and heavy oils the elastic properties of asphalts. For asphaltic residues, the proper balance of asphaltic components and oils is obtained as a result of straight-run distillation under atmospheric pressure or *in vacuo*. For non-asphaltic crudes the proper concentration of asphaltic components in the residuum can be obtained only after an excessive amount of overhead distillates has been taken off. Thus straight-run residues of such crudes are usually oxidized or blown with air under suitable temperature conditions (about 600°F) to increase the proportion of resins and asphaltenes by oxidation and condensation of oily constituents.

Cracked residues, properly distilled or blown, also may form commercial asphalts. "Cracked" asphalts, however, are less homogeneous than straight-run asphalts, due to the presence of carboids and asphaltenes of a lesser degree of dispersion.

Natural asphalts (this term is used with respect to the bituminous portion of natural asphalts, which usually contain a considerable proportion of mineral constituents) have properties and composition very similar to those of petroleum asphalts.

As a result of the high concentration of asphaltic components, the asphalts have a considerable percentage of oxygen and sulfur. Table 148

gives the percentage of sulfur in various petroleum and natural asphalts. The sulfur content is usually greater in the latter than in the former. It should be mentioned, however, that sulfurization of petroleum asphalts or digestion of such asphalts with sulfur does not change or improve the properties of the asphalts treated.

The content of oxygen in petroleum asphalts varies from 2 to 8 per cent. Asphalts rich in sulfur are poor in oxygen, and *vice versa*. It should be mentioned that the per cent of oxygen is usually determined by the difference between 100 and the sum of the other elements including carbon, hydrogen, and sulfur. The percentage of nitrogen is assumed to be negligible. However, in some asphalts it might be 0.5 per cent or more (*e.g.*, California asphalts).

The asphaltic components of straight-run residual asphalts were preformed in crude oils and are merely concentrated in the residues. The asphaltic components of cracked asphalts may be formed partially from virgin asphaltic components, particularly from virgin neutral resins. The neutral resins may be transformed into asphaltenes and then into carboids under cracking conditions. On the other hand, the asphaltic components of cracked residues and asphalts may be newly formed as a result of condensation of polycyclic hydrocarbons. Even purely paraffinic charging stocks, such as butane or paraffin wax, yield asphaltic products in advanced stages of cracking through the intermediate formation of aromatic hydrocarbons.

Table 149 gives the composition of asphaltic residues produced on cracking a Balachany straight-run residuum under varied conditions. The asphalts were produced by stripping the synthetic crudes in high vacuum to the same final temperature.

Table 149. Properties of Cracked Asphalts.

Duration of Cracking	32 min.	-425°, 15 atm—		6 hrs. and 2 min.
		1 hr. and 32 min.	3 hrs. and 2 min.	
Sp. gr. at 15°	0.979	1.11	1.19	1.23
Softening point (Kraemer-Sarnov) (°C)	semi-fluid	76	155	170
Asphaltenes(%)	6.3	30.6	58.3	about 70
Resins (%)	24.1	28.0	18.1	...
Oils (%)	71.6	43.6	25.3	...

The data of Table 149 show that the per cent of asphaltenes in cracked asphalts increases with increasing cracking at the expense of other constituents, *i.e.*, of neutral resins and hydrocarbons.

Oxidation of asphalts with air produces neutral resins and asphaltenes; it is of interest that acids are not formed in this process. The increase in the percentage of asphaltenes is the most important result of blowing, and brings about "hardening" of the oxidized residuum. The following data (page 409) relate to the composition of an asphaltic residuum and of a blown asphalt produced from it.

An observation of Mabery and Byerley¹⁸ on the oxidation of an asphalt (m.p. 25°) is of interest. They oxidized the asphalt, to high melt-

ing point asphalts (m.p. 135° to 260°). The content of oxygen in the oxidized asphalts varied irregularly from 1.88 to 2.20 per cent, indicating that the oxygen was merely a condensing agent, so that the oxidation took place mostly according to the second scheme (p. 406).

	Sp. gr. at 20°	Melting point, Kraemer- Sarnov (°C)	Asphal- tenes (%)	Neutral resins (%)	Oils (%)
Asphaltic residuum	0.978	Liquid	13.0	21.3	65.7
Blown asphalt	1.03	100	31.5	20.8	47.7

The composition of petroleum asphalts, *i.e.*, the content of asphaltenes, neutral resins and oils (hydrocarbons), is given in Tables 150 and 151.

Table 150. Properties and Composition of Asphalts.

Source	Melting Point (°C) Ring & Ball	Penetra- tion at 25°	Duc- tility (cm) at 25°	Asphaltenes (%)	Neutral resins (%)	Oils (%)
Mexico, resid.	57	38	76	22	34	44
California, resid.	55	39	>100	4.6	59	36.4
Venezuela, resid.	56	34	>100	16	35	49
Venezuela, blown	60	60	12	20	26	54
Mexico, blown	89	19	5	30.4	17.6	52
Trinidad, natural	65	10	>100	33	35	32

Table 151. Properties and Composition of Asphalts.

Source	Penetra- tion (cm @ 25°)	Sp. gr. at 20°	Duc- tility at 25°	Softening point (°C)	As- phal- togenic acids (%)	As- phal- togenic anhy- drides (%)	Neutral resins (%)	As- phal- tenes (%)	Oils (hydro- carbons) (%).
						0.08			
Venezuela, resid.	150	1.021		42.6	0.19	0.08	52.26	14.14	33.50
Venezuela, resid.	43	1.031	150+	54.0	0.30	0.07	53.39	20.01	26.54
Venezuela, oxid.	153	1.016		43.6	0.25	0.01	57.02	20.45	28.32
Venezuela, oxid.	40	1.021	10	67.0	0.26	0.17	36.90	35.18	26.97
Trinidad	162	1.010		38.5	0.44	0.12	62.78	4.58	30.89
Trinidad	45	1.024	150+	50.0	0.46	0.24	54.48	14.31	28.70
Smackover, resid.	156	1.017		42.6	0.18	0.19	64.65	9.13	24.54
Smackover, resid.	32	1.033	150+	57.2	0.22	0.21	61.92	13.96	21.63
Smackover, oxid.	183	1.000		42.8	0.41	0.14	45.13	22.29	31.58
Smackover, oxid.	36	1.014	4	82.5	0.25	0.22	32.76	30.39	35.62
Cracked, Dubbs	132	1.058		40.8	0.43	0.41	35.22	22.18	40.98
Cracked, Dubbs	75	1.056	150+	47.0	0.30	0.12	37.24	34.66	27.00

The data of Table 150 by Wilhelmi⁸⁷ and of Table 151 by Wintercorn and Eckert⁸⁹ are not quite comparable in view of some difference in the analytical methods used. Wilhelmi precipitated asphaltenes with ether and Wintercorn and Eckert with normal hexane. The separation of neutral resins by the latter was apparently the more complete.

At the same penetration, the content of asphaltenes in oxidized asphalts is greater than in residual ones, at the expense of neutral resins. This results in lower ductility of oxidized asphalts as compared with residual at the same penetration.

The hydrocarbons of asphalts were investigated by ring analysis by

Grader.⁹ He found that those of natural asphalts are predominantly cyclic and contain only a small proportion of paraffinic side chains, while those of petroleum asphalts are more paraffinic. Mexican asphalts are closer to natural asphalts as far as the percentage of paraffinic side chains is concerned.

The content of carboids, asphaltenes, neutral resins and oils (hydrocarbons) in petroleum asphalts predetermines the basic structure and various physical properties, including penetration, ductility and melting point. The chemical properties of asphalts, especially their stability toward oxidation, are not correlated with the composition, expressed in the terms of the Marcusson analysis. As a matter of fact, oils and neutral resins of different origin may differ in their oxidizability.

The hardening of asphalts with age and in the mixing operation is closely related to oxidation. The hardening is accompanied by the loss of penetration and ductility, resulting in the brittleness of the asphalt and in road failures. Apparently it is caused by the excessive formation of asphaltenes at the expense of neutral resins and hydrocarbons. Cracked asphalts are more susceptible to hardening than straight-run asphalts, obviously because of the less saturated nature of the oils and perhaps the neutral resins. Anderson *et al.*¹ developed the test method of oxidation of asphalts by oxygen, and Ebberts⁸ by potassium permanganate. These tests show that the degree of oxidation is much higher for cracked than for straight-run asphalts.

Structure of Petroleum Residues and Asphalts

The main components of liquid petroleum products are completely miscible and form true and homogeneous solutions. To such completely miscible components belong all hydrocarbons, with the exception of solid petroleum waxes, and all oxygen and sulfur compounds, with the exception of asphaltenes and carboids. The structures due to the presence of petroleum waxes were discussed in Chapter 6; the structures of asphaltic products are described below.

Asphaltic products containing a large proportion of neutral resins and no asphaltenes can be very viscous, but they are homogeneous solutions due to the properties of neutral resins mentioned in this chapter. Thus, the solvent tars, produced by solvent treatment of distillates and containing only neutral resins in addition to hydrocarbons, are homogeneous.

On the contrary, the asphaltic products containing asphaltenes and carboids are non-homogeneous. As stated above, the degree of dispersion of asphaltenes depends upon two factors: the properties of the asphaltenes themselves and those of the petroleum products in which they are dispersed. The asphaltenes, soluble colloiddally in such solvents as benzene or chloroform, are easily dispersed in petroleum products containing neutral resins and aromatic hydrocarbons, by which they are peptized. This colloidal dispersion is stable. Such systems appear to be homogeneous under a microscope and do not flocculate on standing. The addi-

tion of lyophobic hydrocarbons, such as paraffins, however, makes these systems unstable and causes flocculation.

Thus, the structure of a residuum or asphalt containing asphaltenes may be (1) a colloidal solution, if the product contains a large proportion of neutral resins and aromatics, (2) a fine suspension, if it contains also lyophobic hydrocarbons (such as naphthenes with long paraffinic side chains), or (3) a rough suspension, if the product is rich in lyophobic components.

The carboids, which are insoluble in benzene, are not peptized by neutral resins and aromatics and thus form a suspension under any conditions. The inhomogeneity of such products can be easily detected under a microscope or by the so-called Oliensis test.

The asphaltic products containing asphaltenes are: heavy asphaltic crude oils, straight-run residues of asphaltic crude oils, solvent tars produced by treatment of residues, cracked residues, and various petroleum asphalts. Neither asphaltic crude oils nor asphaltic straight-run residues contain carboids. The concentration of neutral resins and aromatics is usually very high in such crude oils and residues. As a result, the asphaltenes present are properly peptized and form a colloidal solution. The petroleum asphalts produced from straight-run asphaltic residues by reduction or oxidation usually have the same structure. They contain a large proportion of asphaltenes (from 10 to 40 per cent) which, having adsorbed resins and aromatics, swell and form a plastic, semi-solid structure. Such a structure is obviously due to the absence or to an insufficient amount of non-adsorbed liquid constituents which otherwise would form a liquid colloidal solution of asphaltenes.

Blending straight-run asphaltic residues with various heavy distillates of reasonably high boiling range usually does not flocculate the asphaltenes. Even in such blends the amount of neutral resins and aromatics is usually sufficient to peptize the asphaltenes and to keep them in a state of colloidal solution. However, blending the heavy asphaltic residues with light paraffinic distillates may partially flocculate the asphaltenes.

Blending cracked residues with straight-run distillates has a flocculating effect. Batchelder² and Batchelder and Wellman³ showed that the aromaticity or aniline point of blended gas oils predetermines the effect of blending. A virgin gas oil of aniline point 154°F admixed with a cracked residuum notably increased the inhomogeneity and deposition of "sludge" on standing; a cracked gas oil of aniline point 104.5°F increased it to a much less extent; another gas oil of aniline point 86°F did not affect the deposition of "carbon"; and a solvent extract of aniline point 31°F markedly reduced it. Plummer^{25a} recommended suppression of the sludge formation in mixtures of cracked residues and distillates by incorporation of the polycyclic aromatic hydrocarbons formed by hydroforming, catalytic cracking etc. The aromatics shall have a specific dispersion greater than 200-250 for F and C spectrum lines.

The cracked asphalts are less homogeneous than straight-run products

due to the presence of carboids and asphaltenes which coagulate more easily than those of straight-run products. Cracked asphalts frequently yield a comparatively large proportion of carbenes, *i.e.*, asphaltenes insoluble in carbon tetrachloride, and from 0.1 to many per cent of carboids insoluble in benzene.

As in the case of cracked residues, the homogeneity of cracked asphalts may be improved by the addition of some highly aromatic materials which stabilize the colloidal particles present in asphalts. Dengler, Gardner and Felder⁷ claim that the mixing of cracked asphalts with an air-blown uncracked asphaltic residue increases the homogeneity of the asphalts. For instance, equal parts of a cracked residuum of specific gravity 1.065 and of an uncracked residuum from Mexican crude with a softening point of 102°F were blended, resulting in an increase in solubility in carbon tetrachloride from 94 per cent for the cracked residuum to 99.6 per cent for the blend. The product, by blowing with air or by reducing with steam, gave high-quality asphalts. The poor solubility (90 per cent) of cracked asphalts in carbon tetrachloride may be increased to 99.8 per cent by this method of stabilization with air-blown uncracked residues.

Thus, the structure of heavy residues and petroleum asphalts may be as follows:

- (1) True solution of hydrocarbons and neutral resins in the absence of asphaltenes.

- (2) Colloidal solution of asphaltenes in hydrocarbons and neutral resins.

- (3) Fine suspension and colloidal solution of asphaltenes in hydrocarbons and neutral resins.

- (4) Suspension of carboids and asphaltenes and colloidal solution of asphaltenes in hydrocarbons and neutral resins.

The above structures may be complicated by the presence of petroleum wax which forms structures discussed in Chapter 6. These structures are superimposed on the above mentioned colloidal or suspension structures.

Petroleum Coke

Petroleum coke may be considered as an ultimate condensation product of petroleum residues and asphalts. Depending upon the temperature-time conditions of the coking process, the percentage of hydrogen in petroleum coke varies in a comparatively broad range from 7 or 8 to 1 per cent. In addition to hydrogen, petroleum coke contains oxygen, sulfur, and nitrogen, the total of which usually varies in the same range. Thus the percentage of pure carbon in petroleum coke would vary from 80 to 97 per cent.

Petroleum coke is insoluble in such solvents as benzene or carbon disulfide.

The petroleum coke formed in the reaction chambers of cracking

units has a maximum amount of "volatiles," or organic compounds decomposed at high temperatures and, correspondingly, a minimum amount of pure carbon. The coke of coking chambers is richer in carbon and that from aromatization or gasification of petroleum at very high temperatures up to 800° (1472°F) is richest in carbon.

The petroleum coke produced under moderate temperature conditions may have a structure intermediate between that of asphalts and of metallurgical coke. The coke of coking chambers has the same structure as conventional coke, *i.e.*, minute graphite crystallites surrounded by still undecomposed polycyclic aromatics, which may disappear almost completely at very high temperatures of coking. Berry and Edgeworth-Johnstone^{3a} recently discussed the problems pertaining to its structure.

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Chapter 10

Classification of Crude Oils

Geological Identification of Crude Oils

From the geological standpoint, the crude oils are identified by productive sands, sandstones and limestones. It is reasonable to expect that a given oil-bearing sand would contain a reasonably uniform crude oil, that is to say, of uniform chemical and fractional composition. Some minor deviations from the average, however, are possible due, *e.g.*, to the changing gas factor (Chapter 1), to the local factors affecting the saturation of the crude oil with gas, to the adsorption effect of clay beds, etc. May, Miners and Spinks⁴ studied the crude oils produced from six wells of the Turner Valley oil field (Lower Cretaceous) in an area of about 50 square miles. The refractive index of narrow fractions versus the boiling range gives about the same curve for all six crudes, with minor deviations. Hendrickson, Hutcheon and Spinks¹ determined the content of benzene, toluene and xylenes plus ethylbenzene in the above crude oils and found that benzene varied from 0.33 to 0.63 per cent, toluene from 1.34 to 2.05 per cent, and xylenes plus ethylbenzene from 1.71 to 2.05 per cent. These deviations may be considered as comparatively small, considering the difficulties involved in the separation of narrow fractions and the analytical determination of hydrocarbons.

In many cases the fractional and chemical compositions of crude oil from the same producing sand are identical or almost identical in fairly distant pools. For instance, the most prolific Woodbine sand (Cretaceous) in the East Texas field produces crudes which are practically identical, varying in the narrow range of specific gravity from 0.825 to 0.835 and of sulfur content from 0.25 to 0.40 per cent, the other properties also being very similar. Moreover, the Woodbine crude oils from other oil fields close to the East Texas field differ from the above type to only a small extent: the Van Zandt crude from the same sand (60 miles to west) has a somewhat higher specific gravity (about 0.865) and a higher sulfur content (0.90 per cent); the Haynesville crude (Woodbine sand, 100 miles to east) has specific gravity 0.845 and sulfur content 0.30 per cent; the other properties of the two crudes are very similar to those of the East Texas field.

The Ordovician Wilcox sand produces practically identical crude oils in the fields of Oklahoma City, Marshall, Tonkawa, Okmulgee, and Ponca City (specific gravity 0.830 and sulfur content 0.2 per cent), while the crudes from the same sand in Seminole and Yale are of some-

what higher specific gravity and sulfur content, being, however, very similar to the crude oil mentioned above.

In other cases, oil fields which are close together may produce quite different crudes from the same stratum. The crude oils of two Grozny oil fields, the New and Old, are produced from the same tertiary sands, easily identified by *Spaniodontella* and *Spirialis* (Middle Miocene). Notwithstanding the close proximity of the two oil fields (about 10 miles) the crudes are quite different—highly paraffinic in the New Grozny field and highly naphthenic or asphaltic in the Old Grozny field. The Baku oil fields, distributed on the small area of the Apsheron peninsula, have a series of productive strata in Pliocene and Upper and Middle Miocene, which may produce quite different crudes from the same sand in different pools.

Different oil-bearing sands of the same pool may produce similar as well as quite different crudes. The productive strata of the Pennsylvania fields are in the range of Devonian to Pennsylvanian formations (Carboniferous), and commonly produce crude oils which are very similar in respect to chemical and fractional composition.

On the contrary, the Russian oil fields, with many producing sands, may give quite varied crude oils in different sands of the same pool. As mentioned above, the Baku oil fields have numerous productive Pliocene and Miocene strata, *e.g.*, as many as 35 oil-bearing sands in the Bala-chany-Sabunchy field. Some of the sands in the same pool yield quite similar crudes, whereas in other sands the properties of the crudes may change more or less gradually from stratum to stratum. The Old Grozny field is similar to the Baku fields and produces at least three different types of crude in its 16 producing sands. The New Grozny field has 24 producing sands, all of which yield almost identical crudes with a high content of paraffin wax.

Thus geological identification of crude oils requires identification of both the oil field and the stratum (sand). Unfortunately in commercial practice crudes are identified by the oil field only; such designations as, for instance, East Texas or Oklahoma City, accepted in this book, would be insufficient if many producing sands were exploited in these fields. As a matter of fact, however, it is chiefly one producing stratum that is exploited, at least for the time given. Thus "East Texas crude oil" means the crude oil produced from the Woodbine sand in East Texas; "Oklahoma City crude oil" means the crude produced from the Wilcox sand in Oklahoma City, etc. Identification of Californian and Russian crudes is more difficult because several oil-bearing strata are exploited. Such designations as, *e.g.*, "Light or Heavy Santa Fé Springs crude oil" show that the crudes are produced from different sands of the field.

There is no clear-cut relationship between the chemical composition of oils and their geological age or origin. It is frequently accepted that those which are geologically old, *i.e.*, Devonian and Carboniferous, are paraffin- and mixed-base crudes, while those geologically new, such as

Cretaceous or particularly Tertiary, are naphthenic or asphaltic. This generalization is more or less valid (with notable exceptions, however) insofar as the crude oils of the United States are concerned, but it seems to be untrue for oil fields of other countries. The tertiary producing strata of Caucasian, Roumanian and Polish fields yield asphaltic, naphthenic, and paraffinic crudes. In California, crude oils in the same pool are usually heavier and more asphaltic from the upper sands than those from the lower sands, according to the above generalization, whereas in Baku the opposite phenomenon is usually observed.

Commercial Classifications

The classification of crude oils should be based on their chemical composition; any other classification based, for instance, upon the specific gravity or fractional composition, would be artificial and misleading. According to the classification commonly accepted in the United States, crude oils are divided into two main groups: paraffin-base and asphaltic-base, depending upon the content of paraffin (petroleum) wax or asphalt, which can be easily determined.

From the commercial standpoint, true paraffin-base crudes on refining yield paraffin wax and no asphalt, whereas true asphaltic-base crudes yield no paraffin wax but are rich in asphalt. The distinction between the paraffin- and asphaltic-base crudes is, however, more fundamental than might be expected on the basis of the content of paraffin wax or asphaltic components. As is well known, the presence of petroleum wax determines in general the "paraffinic" properties of all fractions, and, *vice versa*, a high asphaltic content is responsible for the so-called "naphthenic" properties of all fractions.

While the distinction between the paraffin- and asphaltic-base oils is sufficiently sharp, it should be kept in mind that most crudes do not belong distinctly to either of these two types. Accordingly, the third type, the "mixed-base," includes all oils having intermediate properties. This is the weak point of the classification, since practically 90 per cent of petroleum of various properties and chemical composition is included in the broad and indefinite class of "mixed-base" crudes.

The asphaltic-base class is frequently designated as "naphthenic-base," in view of a misconception which was widely accepted a few years ago. It had been assumed that the paraffinic-base crudes not only contain paraffin wax, *i.e.*, solid paraffin hydrocarbons, but consist almost entirely of paraffin hydrocarbons. In contrast to this, the asphaltic-base crudes were assumed to consist predominantly of cyclic or "naphthenic" hydrocarbons. Accordingly, the mixed-base crudes were assumed to comprise a mixture of paraffinic and naphthenic hydrocarbons. As shown in Chapter 4, such an over-simplification is entirely unfounded. Strange to say, this misconception has survived up to the present time in some petroleum and chemistry handbooks.

Smith and Lane⁶ have given some quantitative foundation to the

commercial classification. In addition to this, the indefinite mixed-base class was subdivided into two narrower groups or classes. The classification was based upon the specific gravity of the fractions boiling between 250° and 275° or 482°-527°F (Key fraction 1) and the cloud point of the fraction boiling between 275° and 300° (527°-572°F) at 40 mm pressure (Key fraction 2).

It is assumed that the specific gravity and cloud point of the Key fractions predetermine the "paraffinicity" of the crude oil, *i.e.*, the percentage of paraffin hydrocarbons, paraffinic side chains, and paraffin wax. By "paraffinicity" is meant the general paraffinic character of the crude oil, caused by the presence of paraffinic hydrocarbons and long paraffinic side chains which are responsible for the low specific gravity and refractive index of the fractions. High values of specific gravity or refractive index are due to cyclic hydrocarbons.

The base of the crude oil is determined from the Key fractions as follows:

If the gravity of Key fraction 1
(at 60°/60°F) is

0.8251
40° API
or lighter

0.8597-0.8256
33.1°-39.9° API

0.8602
33° API

0.8602
33° API
or heavier

and the cloud point of Key
fraction 2 is
the base of the crude is

above 5°F
paraffinic

above 5°F
intermediate

above 5°F
hybrid

below 5°F
naphthenic

Later, Lane and Garton³ developed another classification on the basis of the specific gravity of both Key fractions 1 and 2. The specific gravity of Key fraction 1 predetermines the base of lighter fractions of the crude; that of Key fraction 2 does the same for heavier fractions. For many crudes the base of both key fractions may be the same, and for others may be different, involving new types and classes of oils. Thus, crude oils may be paraffinic in low-boiling fractions and "naphthenic" in high-boiling fractions, and vice versa.

Thus the new classification divides the crude oils into 9 classes or bases: paraffinic-paraffinic (or paraffinic), paraffinic-intermediate, paraffinic-naphthenic, etc. The classes paraffinic-naphthenic and naphthenic-paraffinic have not been recognized in any existing crude.

A serious shortcoming of any classification based on the specific gravity (or any other physical property) of fractions is the fact that the high specific gravity may be due to the presence of naphthenic and aromatic hydrocarbons. Actually, both naphthenes and aromatics are associated in "naphthenic" or cyclic group of hydrocarbons; thus, a great difference between these two types of hydrocarbons has not been reflected in the classification. Moreover, high asphaltic crude oils, rich in sulfur and oxygen compounds, producing fractions of high specific gravity, are also classified as "naphthenic" crude oils. Thus, the class of "naphthenic" crude oils actually includes quite different crudes: aromatic, naphthenic (in the chemical sense of the word), and asphaltic, or various mixtures of these types.

The base of the crude oil is determined as follows:

Gravity of Key fraction 1 API, 60°F	Sp. gr., 60°/60°F	Gravity of Key fraction 2 API, 60°F	Sp. gr., 60°/60°F	Base of crude	
				Light fractions	Heavy fractions
40 or lighter	0.8597 or lighter	30 or lighter	0.8762 or lighter	Paraffinic	Paraffinic
do	do	20.1 to 29.9	0.9334 to 0.8767	do	Intermediate
do	do	20.0 or heavier	0.9340 or heavier	do	Naphthenic
33.1 to 39.9	0.8597 to 0.8256	30.0 or lighter	0.8620 or lighter	Intermediate	Paraffinic
do	do	20.1 to 29.9	0.9334 to 0.8767	do	Intermediate
do	do	20.0 or heavier	0.934 or heavier	do	Naphthenic
33.0 or heavier	0.8602 or heavier	do	do	Naphthenic	do
do		20.1 to 29.9	0.9334 to 0.8767	do	Intermediate
do		30.0 or lighter	0.8767 or heavier	do	Paraffinic

Kraemer and Lane² made an attempt to justify the conventional conception of the "naphthenic-base" crude oils from the chemical standpoint. According to these authors, these crudes really are naphthenic in the chemical meaning of the term, because "aromatic hydrocarbons are rarely present in any great quantity in crude petroleum." Accordingly, Key fraction 1 would consist either of paraffins or naphthenes. "If Key fraction 1 were composed entirely of aromatics its specific gravity would be greater than that of water." These statements are in evident contradiction to the properties of alkylated aromatics, which may be of moderate specific gravity, and to the present status of the chemical composition of petroleum, which undoubtedly does contain a large proportion of aromatics, as well as of resinous and asphaltic components. The conventional designation of all cyclic hydrocarbons and asphaltic components as "naphthenes" invariably leads to confusion and ambiguity, as will be seen shortly.

Application of the correlation index (Bureau of Mines), discussed in Chapter 2, to the classification of crude oils gives more reliable results than the use of the key fractions. Smith⁷ determined the values of C.I. for fractions of various crudes. It will be seen from his data that the paraffin-base crude oils (Bradford, Rodessa, Cotton Valley) are predominantly paraffinic, particularly in low-boiling fractions. In medium and high-boiling fractions the C.I. does not change within broad limits, and does not exceed 25. This shows that the cyclization of hydrocarbons is moderate and is compensated by paraffinic elements, *i.e.*, by paraffin hydrocarbons and paraffinic side chains. The value of the C.I. of 25 or less is characteristic of fractions of paraffin-based crude oils.

The Badarpur crude represents a quite different type. The C.I. of its fractions is high, and changes rapidly, indicating a rapid increase in the

cyclization of the fractions. The content of paraffinic elements is low. The high-boiling fractions apparently are highly aromatic and polycyclic.

Although the C.I. method gives a clear chemical picture of the crude, the method has the inherent shortcoming of any method based upon the physical properties of petroleum. While the low values of the C.I. (below 25) indicate the predominance of paraffinic elements, values of about 50 or more may be due to the presence of naphthenes, aromatics, and neutral resins (in high-boiling fractions) with paraffinic side chains of varied length. The C.I. value does not indicate even the approximate proportion of the above constituents, which predetermine the properties and classification of non-paraffinic crude oils.

Chemical Classification

An attempt to develop the chemical classification of crude oils on the basis of the content of various classes of hydrocarbons has been made by Sachanen and Virobianz.⁶ The crudes were classified according to the proportion of aromatic, naphthenic, and paraffin hydrocarbons in the distillates. The drawback to this classification was the disregard of resinous and asphaltic compounds which were associated with aromatic hydrocarbons.

A new attempt is being made to classify crude oils on the basis of more complete data on chemical composition available at the present time, including the data of ring analysis. The oils are classified according to the content of paraffinic constituents, *i.e.*, paraffin hydrocarbons and paraffinic side chains, naphthenic and aromatic constituents, and resinous-asphaltic compounds. It should be pointed out that the term "naphthenic" in this classification has the well established chemical meaning, *i.e.*, the saturated cyclic structures (in practice, the five- and six-ring structures, since the presence of other cyclic structures in petroleum has not been proved) and differs substantially from the same term in the classifications discussed above, in which it means the cyclic structure in general, embracing the naphthenic, aromatic and asphaltic structures. It is believed that many misconceptions and shortcomings can be avoided by the use of the classification based on the chemical composition of crude oils. For instance, Kraemer and Lane¹ on the basis of the Key fractions, classified as "paraffin-base" such different crude oils as Pennsylvania (Allegheny county), Panhandle and Pechelbronne. The Panhandle and, particularly, Pechelbronne crudes contain a large proportion of resinous-asphaltic compounds causing, for instance, high carbon residues of residuum (10.9 per cent for Pechelbronne crude vs. 0.6 per cent for Pennsylvania crude). The Pechelbronne crude oil, rich in resinous-asphaltic compounds, evidently cannot be classified with Pennsylvania crudes, which are predominantly paraffinic and very poor in resins and asphalts.

The same authors classified a Ural crude oil as belonging to the "naphthenic" base, whereas it is aromatic-asphaltic, producing highly aromatic

gasoline and other distillates and a highly asphaltic residuum. The content of naphthenes, in the chemical sense of this word, does not exceed 15 per cent.

The Dossor crude oil is classified as "intermediate" base, whereas it is a rare example of purely naphthenic crudes containing 75 per cent of naphthenes.

The figures of the average composition of crude oils given below have been calculated from the data on the composition of various fractions, from gasoline to heavy lubricating fractions and residuum. These data, available for many crudes, are obtained by ring analysis and by the determination of aromatics, naphthenes, paraffins, and resinous-asphaltic constituents (Chapters 2 and 3).

Both methods are applied to determine the chemical class of a crude oil. The ring analysis data are particularly important for determining the paraffinic character or "paraffinicity" of crude oils, since this property depends as much upon the content of paraffin hydrocarbons as upon that of paraffinic side chains. In addition, the percentage of resinous-asphaltic constituents is not determined by the ring analysis. Thus the data obtained by both methods must be used.

Ring analysis data are usually lacking for residues containing a large proportion of neutral resins and asphaltenes. The conversion of the content of the resinous-asphaltic components into ring analysis data has been made on the assumption that the average formula of the resinous-asphaltic components corresponds to that of heavy resins extracted from residues, approximately $C_{60}H_{85}O_3$ (Chapter 9). The tentative structure of this resin would correspond to four tetralin rings, probably with some short paraffinic side chains, connected by oxygen atoms and a number of methylene groups. Such a tentative formula of heavy neutral resins is open to criticism, but it should be pointed out that other probable assumptions would give approximately the same result with reference to the number of rings and paraffinic groups. Under these assumptions, the resinous-asphaltic constituents would contain 40 per cent aromatic rings, 27 per cent naphthenic rings and 33 per cent paraffinic side chains (oxygen being neglected).

The content of paraffin hydrocarbons in residues was accepted as equal to that of solid petroleum wax on the assumption that liquid paraffin hydrocarbons of branched structure are absent in residual oils (Chapter 4). The distribution of aromatics, naphthenic rings and paraffinic side chains in asphalt-free residues was taken to be the same as in the heaviest lubricating fraction for which ring analysis data are available.

The determination of aromatic hydrocarbons by sulfonation gives fairly reliable results for all fractions. The determination of naphthenic and paraffin hydrocarbons is reliable for gasoline and for heavier fractions, in which the content of paraffin hydrocarbons is assumed to be equal to that of petroleum wax. The determination of naphthenes and

paraffins in kerosene and light gas oil distillates on the basis of aniline points or other physical properties is impossible, as has been shown on page 100. A direct determination of paraffins in these fractions is accompanied by many experimental difficulties because of the comparatively low melting points of the paraffins in these distillates. Thus, the content of paraffins and naphthenes in the kerosene and light gas oil fractions was extrapolated from the data for gasoline and heavier fractions.

It should be pointed out, however, that these more or less arbitrary assumptions do not appreciably affect the figures given below. In any case, the possible errors, owing to the assumptions involved, would not affect the general chemical character of a given crude oil nor change its place in the classification.

Paraffinic Crude Oils

The basic chemical classes of crude oils are: paraffinic, naphthenic, aromatic, and asphaltic. Purely paraffinic crude oils of the conventional type, containing mostly paraffin hydrocarbons, are unknown. Natural gas, however, may be considered as a pure paraffinic gaseous crude of the same origin as conventional crude oils. Ozokerite is an almost pure paraffinic bitumen of the same origin. As far as physical properties are concerned, the condensates (from the condensate fields) are closer to conventional crude oils than is natural gas or ozokerite. The proportion of paraffins in the condensates is as high as 75 per cent. The origin of the condensates, however, is different from that of crude oils and is due to the secondary condensation of gaseous constituents accumulated in reservoirs under pressure. For this reason, classification of the condensates with conventional paraffinic crude oils would be ambiguous.

The conventional paraffinic crude oils contain, in addition to paraffin hydrocarbons, a large proportion of cyclic hydrocarbons, predominantly naphthenes, with long paraffinic side chains. This class of crude oils is well defined also in other classifications, because the low specific gravity or C.I. of fractions is characteristic only of paraffin hydrocarbons or of cyclic hydrocarbons with long paraffinic side chains. The chemical composition of paraffinic crude oils may be represented as follows:

Paraffin hydrocarbons (including petroleum wax)	40 per cent (by weight)
Naphthenes	48 " "
Aromatics (sulfonatable)	10 " "
Resins and asphaltenes	2 " "

The paraffinic characteristics of the paraffinic crude oils is concealed to a certain extent by a high percentage of naphthenes which, however, have long paraffinic side chains. The ring analysis gives the following figures for the paraffinic crude oils:

Paraffinic side chains	78 per cent
Naphthenic rings	16 " "
Aromatic rings	

Thus, the paraffinic character of the paraffinic crude oils is shown better by the ring analysis data.

The percentage of paraffinic side chains (75 or more) and C.I. values of 25 or less may be accepted as the identification marks of the paraffinic crude oils.

The paraffinic crude oils are represented in the United States by Pennsylvania, W. Virginia, Rodessa and some other crude oils. It is of interest that the oil fields of other countries do not produce true paraffinic crudes in any substantial quantities.

As has been stated above, the paraffinic character of paraffinic crude oils is manifested in all fractions. Gasoline and naphtha fractions are rich in paraffins, usually of normal or slightly branched structure, resulting in low octane numbers. The kerosene and light oil fractions consist of paraffins and naphthenes with paraffinic side chains of varied length. The high-boiling gas oil and lubricating fractions, including residuum, contain petroleum wax in the amount of about 15 per cent with respect to the wax-bearing fraction. A very high percentage of petroleum wax, however, is not a necessary property of paraffinic crudes. The content of petroleum wax in some paraffinic-naphthenic crude oils may be even higher than in crude oils of the Pennsylvania type, which have a high percentage of wax-free light fractions.

The dewaxed gas oil and lubricating fractions consist mostly of bicyclic naphthenes with long paraffinic side chains, which cause the high viscosity index of these fractions. The content of aromatic hydrocarbons is low in all fractions. The content of resins and asphaltic compounds is low even in residues, resulting in a high commercial value of the residues; thus they require a moderate degree of treatment to be refined to high-quality, viscous lubricating oils.

Another peculiarity of paraffinic crude oils is the high flash point of their lubricating fractions due to the high boiling points of viscous bicyclic naphthenes with long paraffinic side chains, which are present in these fractions, compared with equally viscous polycyclic naphthenes and aromatics with short side chains, which are characteristic of aromatic and asphaltic crudes.

Naphthenic Crude Oils

Another chemically simple class of crude oils is the naphthenic group. Such crude oils are rare, and are represented in the United States only by some California crudes. The only representative of the naphthenic crude oils which has been thoroughly studied is the Emba-Dossor crude oil, the composition of which may be given as follows:

Paraffin hydrocarbons	12 per cent
Naphthenes	75 " "
Aromatics	10 " "
Resins and asphaltenes	3 " "

The ring analysis gives the following data:

Paraffinic side chains	63 per cent
Naphthenic rings	30 " "
Aromatic rings	7 " "

In contrast to the paraffinic crude oils, the data of chemical analysis reflect the naphthenic character of the naphthenic oils better than the data of the ring analysis.

The naphthenic crude oils produce highly naphthenic fractions from gasoline to residuum. The petroleum wax is present in a very small proportion, not exceeding a fraction of one per cent. The naphthenes of high-boiling fractions and residuum have, however, long paraffinic side chains resulting in a comparatively high viscosity index. The content of aromatics and resinous compounds is small. As a result, the residuum can be used as a high-viscosity lubricating oil after light treatment, as in the case of paraffinic crude oils.

Many Baku crude oils are similar to the Emba crudes, but contain a higher percentage of other constituents at the expense of naphthenes. The composition of two such crude oils is given below:

	Balachany	Bibi-Eibat
Paraffin hydrocarbons	9	11
Naphthenes	66	60
Aromatics	19	19
Resins and asphaltenes	6	10

While the Balachany crude oil is close to the Emba crude, the Bibi-Eibat crude is intermediate between the naphthenic and naphthenic-aromatic crude oils. It may not be a coincidence that the naphthenic crude oils are concentrated in the basin of the Caspian Sea.

Aromatic and Asphaltic Crude Oils

The following simple class of crude oils would include the aromatic crudes which contain, say, 50 per cent or more aromatic hydrocarbons. The crude oils of this class are not known. As will be seen later, even Borneo or Perm (Ural) crude oils only approach this class, being less aromatic, and belonging to the mixed classes.

The last simple class of crude oils includes those which consist predominantly of resinous and asphaltic constituents, *i.e.*, of oxygen-sulfur compounds. Crudes of this type are unknown, since the low- and medium-boiling distillates, present in crude oils, consist of hydrocarbons which decrease the percentage of resinous and asphaltic constituents. The natural asphalts or, better, the organic part of the natural asphalts, are bitumina which belong to the class in question. The chemical composition of a natural asphalt (Bermudez, penetration 25) may be represented as follows:

Paraffin hydrocarbons	5 per cent
Naphthenes	15 " "
Aromatics	20 " "
Resins and asphaltenes	60 " "

The liquid hydrocarbons of natural asphalts consist mostly of aromatics and naphthenes, which are polycyclic and have short paraffinic side chains.

As has been stated above, crude oils which are predominantly paraffinic, naphthenic, aromatic or asphaltic are rather exceptional. Usually they contain at least two classes of these constituents which predominate over the others.

Paraffinic-Naphthenic Crude Oils

The paraffinic-naphthenic class is widely distributed. Many Mid-Continent crudes belong to this group, as, for instance, Oklahoma City or East Texas, the approximate composition of which is as follows:

	Per cent by weight	
	Oklahoma City	East Texas
Paraffin hydrocarbons	36	33
Naphthenes	45	41
Aromatics	14	17
Resins and asphaltenes	5	9

The ring analysis gives the following figures:

	Per cent by weight	
	Oklahoma City	East Texas
Paraffin side chains	65	60
Naphthenic rings	25	26
Aromatic rings	10	14

Paraffinic-naphthenic crude oils produce fairly paraffinic gasolines. For instance, the composition of Oklahoma City straight-run gasoline is close to that of Pennsylvania gasolines, whereas East Texas straight-run gasolines are more naphthenic. The content of paraffin wax in the paraffinic-naphthenic crudes may be up to 6 per cent or more. Therefore, the heavy gas oil and lubricating fractions contain a high percentage of petroleum wax, amounting to 10 to 20 per cent. The paraffinic side chains of naphthenes of lubricating oils are shorter, compared with Pennsylvania lubricating oils. As a result, the viscosity index of Mid-Continent lubricating oils is lower (up to 80). As the comparison of the composition of paraffinic and paraffinic-naphthenic crude oils shows, the latter have also a greater content of aromatic, resinous and asphaltic constituents.

Of the two above Mid-Continent crudes, the Oklahoma City is more paraffinic than the East Texas. As in other mixed classes, there is a whole spectrum of paraffinic-naphthenic crudes, from those which are close to paraffinic crudes to those which are close to naphthenic crudes.

Naphthenic-Aromatic Crude Oils

An increase in the content of aromatics at the expense of naphthenes would produce paraffinic-naphthenic-aromatic crude oils, in which the percentage of each of the three classes of hydrocarbons is almost equal. The percentage of resinous and asphaltic compounds in these crudes is near 10 per cent. Crudes of this type are comparatively rare, as, for

instance, Maikop oils. In contrast to these, naphthenic-aromatic crudes are common, particularly those in which naphthenes predominate over aromatics. Many Gulf Coast and California crudes belong to this class. The composition of a light California crude oil (Santa Fé Springs) may be represented as follows:

Paraffin hydrocarbons	20 per cent
Naphthenes	45 " "
Aromatics	23 " "
Resins and asphaltenes	12 " "

The ring analysis of the same crude oil gives the following data:

Paraffinic side chains	48 per cent
Naphthenic rings	30 " "
Aromatic rings	22 " "

Crude oils of the naphthenic-aromatic class are poor in petroleum wax and contain a considerable percentage of resinous and asphaltic constituents. Paraffin hydrocarbons are present mostly in gasoline and light kerosene fractions. Due to a moderate percentage of paraffinic side chains, the naphthenes and aromatics of lubricating fractions have comparatively short side chains, resulting in low values of the viscosity index.

The naphthenic-aromatic crudes with an almost equal content of naphthenes and aromatics may be represented by Borneo crude oil. Its composition (sp. gr. about 0.85) is as follows:

Paraffin hydrocarbons	15 per cent
Naphthenes	35 " "
Aromatics	35 " "
Resins and asphaltenes	15 " "

Mixed Asphaltic Crude Oils

Naphthenic-aromatic-asphaltic crude oils are also widely distributed. Many heavier Coastal and California, as well as Mexican and Venezuelan crudes belong to this class. The composition of a heavy naphthenic-aromatic-asphaltic crude oil (sp. gr. 0.930, Inglewood) is:

Paraffins	8 per cent
Naphthenes	42 " "
Aromatics	27 " "
Resins and asphaltenes	23 " "

The very small proportion of paraffins is partially due to a low content of gasoline and other low-boiling fractions, which are comparatively rich in paraffins. If the crude oil of this class is of low specific gravity and contains a large proportion of gasoline, the percentage of paraffins will be somewhat larger, at the expense of other constituents. The percentage of paraffinic side chains in these classes of oils is small, and does not exceed 40 per cent, indicating short paraffinic side chains and very low (negative) values of the viscosity index of high-boiling fractions.

Aromatic-asphaltic crude oils containing predominantly aromatic and asphaltic constituents occur less frequently than the representatives of

the naphthenic-aromatic-asphaltic class. The Perm (Ural) crude belongs to this class as its composition clearly shows:

Paraffin hydrocarbons	13 per cent
Naphthenes	15 " "
Aromatics	40 " "
Resins and asphaltenes	32 " "

Apparently some heavy Mexican crude oils (*e.g.*, Panuco) have a similar composition.

There are no crude oils which would belong to such mixed classes as paraffinic-aromatic or paraffinic-asphaltic.

As has been stated by Lane and Garton, some crude oils may have a different chemical character in low-boiling and in high-boiling fractions. In extreme cases, a crude oil may be paraffinic in low-boiling and aromatic or asphaltic in high-boiling fractions, or, *vice versa*, aromatic in low-boiling and paraffinic in high-boiling fractions. In such cases the average chemical composition would give only the general and average picture. The method of Lane and Garton may be applied also to the chemical classification developed in this chapter, *i.e.*, the chemical composition may be determined separately for lighter fractions, including gasoline, kerosene and light gas oil, and for heavier fractions, including

Table 152. Classification of Crude Oils.

Class	Composition	Crude Oils
Paraffinic	Percentage of paraffinic side chains 75 per cent or more	Pennsylvania, Rodessa
Naphthenic	Percentage of naphthenic hydrocarbons 70 per cent or more	Emba-Dossor
Aromatic	Percentage of aromatic hydrocarbons 50 per cent or more	None
Asphaltic	Percentage of resins and asphaltenes 60 per cent or more	(Bitumina of natural asphalts)
Paraffinic-naphthenic	Percentage of paraffinic side chains from 60 to 70; percentage of naphthenic rings at least 20	Many Mid Continent crude oils
Paraffinic-naphthenic-aromatic	Percentage of paraffins, naphthenes and aromatics approximately equal	Maikop
Naphthenic-aromatic	Percentage of naphthenes or aromatics 35 per cent or more	Light Coastal and California crude oils
Naphthenic-aromatic-asphaltic	Percentage of naphthenes, aromatics, or asphaltic compounds 25 per cent or more	Heavy Coastal and California crude oils
Aromatic-asphaltic	Percentage of aromatics or asphaltic compounds 35 per cent or more	Ural, Probably some heavy Mexican crude oils.

heavy gas oil, lubricating fractions and residuum. It should be pointed out, however, that the above-mentioned extreme cases actually have not been found. In most cases the chemical characteristics of crude oils change gradually from light fractions, more paraffinic, to heavier fractions and residuum, more naphthenic, aromatic and asphaltic. This gradual change is reflected in the average chemical composition of crude oils. In rare cases the paraffinicity of fractions may increase with boiling

range, as, for instance, for Surachany or Van Zandt crude oils (Chapter 4).

Table 152 summarizes the most important and frequent classes of crude oils. All existing crude oils may be classified in seven chemical classes or types.

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